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Initial stage of formation of a metal-semiconductor interface: Al on GaAs(110)

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A re-examination of the experimental data and previous electronic structure calculations on the prototype system Al/GaAs(110), together with new calculations and models, indicates that at low coverages and temperatures neither a covalent bond nor a metallic bond is formed between Al and the substrate. Instead, the predominant species is likely to be Al clusters which interact only weakly with the substrate.

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The understanding of the changes in the low-temperature electronic and structural properties of a clean GaAs surface upon deposition of submonolayer amounts of simple metal atoms (e.g., Al) has long been recognized as central to the understanding of chemisorption-induced surface chemistry and Schottky barrier formation in heteropolar semiconductors.[1-9] A large diversity of theoretical methods have been applied to the problem,[1-6] all attempting the interpretation of the experimental data on the prototype system GaAs(110)/Al in terms of the formation of either metallic bonds[1] or an epitaxially ordered array of directional covalent bonds between the adatoms and the substrate atoms.[2-6] The bonded ordered overlayer model, if correct, leads to the prediction of profound changes in the core and valence states of the semiconductor,[1-6] often accompanied by substantial surface relaxation.[3-4] It also results in the identification of the Fermi level pinning states as arising from such chemisorptive bonds. In this paper I show that a re-examination of the experimental data and 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 room temperature deposition of Al on GaAs(110) the Al atoms do not bond to either Ga or As. Instead, in sharp contrast with all previous models,[1-6] it is shown that the Al atoms are likely to bond predominantly among themselves, forming Al_n molecular clusters which interact only weakly 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),[7] the present model suggests that pinning of the Fermi energy may not be induced by chemisorptive bonds. Pinning by defect levels[7] is then a possible mechanism. This new model leads to a number of interesting predictions on the surface atomic structure and its spectroscopy.

We start by considering the theoretical models that assume the formation of *metallic* adatom–substrate bonds, simulated by a thick layer (15–20 Å) of jellium in contact with an abrupt, unrelaxed surface.[1] Experimental evidence from photoemission studies suggests that the barrier heights are already developed at less than $\frac{1}{2}$ ML coverage[7] and that no gap surface states (expected from an ideal unrelaxed surface) appear at the early stages of deposition.[7,9] In addition, LEED studies show the same intensity patterns as observed in the clean (i.e., relaxed) surface[7] (with additional increased background indicating a disordered adlayer). This shows that the proper theoretical model for testing the relevance of metallic bonding hypothesis is a *thin* ($<\frac{1}{2}$ ML) jellium layer on a *relaxed* surface. Our self-consistent pseudopotential calculation shows that under these conditions no Fermi level pinning metal-induced gap states occur. (Such an ultrathin "metallic" layer is not even a metal.) Hence, while the thick jellium model[1] has yielded results which 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 where they are formed.

Consider next the theoretical models that assume an epitaxial *covalent* bonding of Al to the substrate atoms. With the exception of the Hartree–Fock (HF) cluster models,[6] all such calculations[1-5] assume an Al–Ga or Al–As bond length taken from the bulk materials (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.

The adsorbed Al atom has a monovalent s^2p^1 configuration [denoted Al(I)], which differs from the multicoordinated promoted s^1p^2 form [denoted Al(III)] characteristic of the tetrahedrally bonded bulk material. This has a significant implication for the bond lengths: Examination of the heats of formation of column III halides indicates that whereas at the top of the column the trivalent form is far more stable than the monovalent form [e.g., in kcal/mole, $\Delta H(BF) > 0$, $\Delta H(BF_3) = -271.4$; $\Delta H(AlF) = -63.4$, $\Delta H(AlF_3) = -289.0$], at the bottom of the column, as the paired s electrons become farther removed from the outer p-shell, the stabilities of the two forms become closer [e.g., for the solid phases, $\Delta H(TlF) = -77.8$, $\Delta H(TlF_3) = -136.9$]. This pattern is readily understood in terms of the increase in energy required to promote the monovalent s^2p^1 to the trivalent s^1p^2 form; atomic total energy calculations[10] yield 2.7, 3.3, and 4.7 eV for B, Al, and Ga, respectively. This has an immediate implication for the bond lengths: 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) vs the X-atom electronegativity

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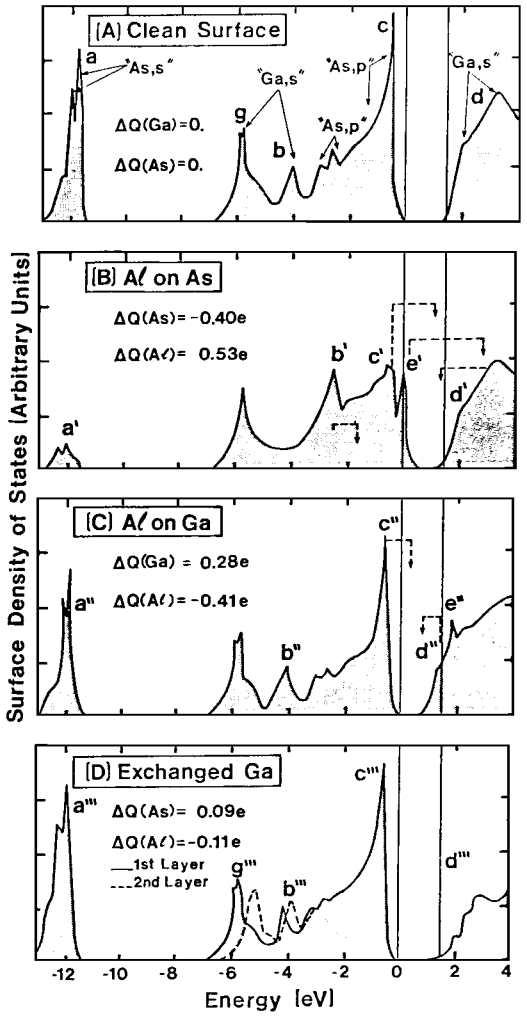

FIG. 1. Smoothed surface density of states for different chemisorption models of Al on GaAs(110).

yields an Al(I)–Ga bond distance of 3.1 Å, far larger than that previously inferred from Al(III) bulk data.[1–5] A cluster-type HF calculation for Al(I) bonded to Ga in $GaAs_2$ indeed yields d(Al–Ga) = 3.04 Å (and a binding energy of 0.4–0.6 eV[6]). Since the two-center matrix elements $H_{ij}(d)$ appearing in surface calculations[1–5] scale approximately as d^{-2}, the use of d = 2.43 Å rather than d = 3.1 Å (an error of a factor 0.6 in H_{ij}) makes the previous conclusions on GaAs/Al unreliable.

This analysis and the finding indicated in Ref. 10 suggest the undertaking of new quantitative self-consistent calculations. Using the distances d = 2.8, 3.0, 3.2, and 3.4 Å and a relaxed surface geometry, a total energy minimization[10] was performed 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). This yielded at equilibrium d(Al–Ga) = 3.1 ± 0.1 Å and d(Al–As) = 3.0 ± 0.1 Å, in reasonable agreement with our estimates but in disagreement with the values (d = 2.43 Å) assumed in previous calculations. Figure 1 shows the predicted one-electron spectra at equilibrium. The dashed arrows point to the positions of the main peaks obtained in previous calculations. We analyze these spectra below and show that they conflict with experiment. We then introduce the Al_n–GaAs(110) cluster model.

A(I) bonded to As [Fig. 1(b)]: (i) b' is an A(I)–Ga s-state, localized on the adatoms A(I) and shifted to lower binding energy relative to the clean surface [Fig. 1(a)] Ga states g and b.[11] The calculated shift $\Delta_{b'g}$ is 2.8 eV for A = Al (3.5 eV for d = 2.43 Å[4]), 1.8 eV for A = Ga[3] and 1.5 eV for A = In.[5] The corresponding atomic energy difference[10] $\Delta\epsilon_{ss} = \epsilon$[Ga(III)] $- \epsilon_s$[A(I)] is 2.8, 1.6, and 1.3 eV for A = Al, Ga, and In, respectively, confirming the identification of b' as localized state. Experimentally, one finds $\Delta_{b'g}$ to be 1.5 eV for In (binding energy of $E_{b'} = -5$ eV)[5] and 0.9–1.3 eV for Ga ($E_{b'} = -5.6$ eV).[3] For Al, which is expected to have the largest shift, no shift has been observed by Spicer *et al.*[7] and Huijser *et al.*,[9] whereas Chadi and Bachrach[3] found a weak structure at $E_{b'} = -6.1$ eV ($\Delta_{b'g} \sim 1.5$ eV) which was not reproduced in the other experiments.[7,9] However, even if experimentally $\Delta_{b'g} \neq 0$ for Al, the order of the observed binding energies $E_{b'} = -6.1$, -5.6, and -5 eV for Al, Ga, and In, respectively, is reversed to that obtained both in the surface calculations and from the atomic estimates. (ii) The peak c' is an As–A(I) p-like dangling bond state replacing the clean surface As state c. Experimentally, one does not observe any strong attenuation of c nor the appearance of a new peak c' upon deposition of Al, Ga, or In.[5,7–9] (iii) 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 CBM for d = 2.43[2] and d = 3.1 Å, respectively. The tight binding (TB) model,[3,4] failing to include any direct interadatom interactions, places e' above d' and hence leads to a fundamentally different pinning mechanism. Experimentally,[7–9] 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 two orders of magnitude (e.g., due to averaging over a number of surface layers) to explain their absence in the observed spectra.

A(I) bonded to Ga [Fig. 1(c)]: The major differences with the previous case are (i) the peak b'' is unshifted but has a somewhat increased intensity. (ii) The cation p-like bonding state d'' is now stabilized by bonding of A(I) to Ga and appears in the gap below e'', predicting pinning at much too low energies: 0.4 eV below CBM for d = 3.1 Å (observed value: 0.8–1 eV). Due to its two-center (A–Ga) nature (and resulting mixed angular momentum content) and substantial intensity, matrix element effects are not expected to reduce its strength 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[7]; the Ga 3d exciton is unshifted in energy and unchanged in shape upon Al deposition.[7,9]

The inserts 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 are used in the discussion below). In case 1B (negatively charged Al) one expects a shift of the As (Al) core states to higher (lower) ionization energies whereas in situation 1C (positive Al) the

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As (Al) core states are expected to shift to lower (higher) ionization energies. In contrast, Huijser *et al.*[9] have found that for $\sim\frac{1}{3}$ ML of Al deposited at room temperature, the substrate core emission and the surface sensitive core exciton are weakened in intensity but remain unshifted relative to the clean surface. The significant point here is that all theoretical models that assume either an adatom–substrate covalent bond [Figs. 1(b), (c)] or a metallic bond predict a charge exchange between the substrate and adlayer and that this transfer has an opposite sign on both sides of the interface. These models hence lead inevitably to (substantial[4,6]) core shifts, in opposite directions, in sharp conflict with experiment.

The long adatom–substrate bond distances suggest that bonding of Al(I) to the substrate is likely to be unstable towards formation of Al clusters: bonding to any of the semiconductor sites results even at $\frac{1}{2}$ ML in a very large Al–Al separation of 3.96 Å (next nearest neighbor substrate distance) and small binding energy $BE \sim 0.4$–0.6 eV,[6] well outside the stability range of Al systems: for metallic Al and Al_2[10] respectively, d(Al–Al) = 2.86 and 2.50 ± 0.1 Å and BE = 3.4 and 0.85 ± 0.15 eV. 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 clusters Al_n. As one moves down column III (e.g., to In[5], Tl), a singly coordinated bond to the substrate is likely to be initially favored over inter-adatom bonding.

This model has a number of interesting predictions, all of which are in conflict with the ordered covalent bonding model: (i) As observed,[7–9] the spectral features of the substrate will be similar to those of the clean surface, lacking the sharp structures characteristic of covalent chemisorptive bonds. (ii) Since the molecular clusters Al_n interact only weakly and largely nondirectionally with the substrate, the adlayer will be disordered above a translational freezing temperature, as indeed observed by LEED. (iii) Clusters with (Poisson distributed) small values of n will reside in the (110) surface troughs which have their base on the second subsurface layer; under conditions where chemical exchange occurs with the substrate cations (see below), *second layer* atoms will be exchanged. This should be detectable by LEED. (iv) The core energy levels of the Al_n clusters (e.g., $2p$) will occur *above* the bulk metallic value (72.6 eV) but *below* the value expected for Al–Ga or Al–As bonds (74–75 eV, interpolated from data on nine AlX compounds). Further, whereas the covalent bonding model predicts the latter value to remain constant as the coverage increases from 0.1 to 1 ML (more of the same Al-substrate bonds formed), the present model predicts this energy to change as the average n value attained at a given temperature and coverage increases from small n (covalent clusters) to $n \geq 100$ (metallic drops) and finally to coalesced continuous layers. This is precisely what is observed experimentally.[7] (v) The spectral features above VBM and below E_F will be characteristic of cluster states (not chemisorption bonds), much like those calculated[12(a)] and observed[12(b)] for small transition atoms and Al clusters on a covalent substrate. It would be interesting to determine spectroscopically the transition from molecular ($n < 100$) to free-electron-like cluster levels. (vi) No low-temperature low-coverage epitaxy of Al will be formed on the (110) plane whereas such an epitaxy is possible on an (100) face.

When the Al/GaAs(110) is heated[9] (or prepared at room temperature with more reactive substrates[3,8]), the thermal energy and lateral spreading pressure overcome, eventually, 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 (full line) and when the first two Ga layers are exchanged (dashed line); the exchanged Ga is assumed to escape.[9] The main effects are: (i) The high-energy tail of the second-layer cation state g''' is shifted from its surface counterpart g, increasing somewhat the heteropolar gap (a–g) with respect to GaAs.[9] (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[3,5,7] (and expected from atomic estimates $\Delta\epsilon_{ss} = \epsilon_s[\text{Ga(III)}] - \epsilon_s[\text{Al(III)}] = 1.4$ eV); and (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. 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 at high coverages (>2 ML[3,8]) or for low-coverage heated surfaces.[9] I conclude, therefore, in agreement with Ref. 4 that these results pertain to exchanged Ga and not to chemisorbed Al.[1–2,5]

More details on the cluster model are discussed elsewhere.[13]

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