Surface-Barrier Formation for Al Chemisorbed on GaAs(110)

Eugene J. Mele
Xerox Webster Research Center, Webster, New York 14580

and

J. D. Joannopoulos
Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

(Received 29 January 1979)

Using a localized orbital theory, we have studied the electronic and electrical properties of Al chemisorbed on GaAs(110). We find that both the microscopic data and the macroscopic induced barrier are fully explained by the electronic structure of a new Al-As-Ga complex on the surface. This complex results from an exchange reaction in which Al replaces the surface Ga and an unexpected structural relaxation induced by the chemisorption of the metal.

The microscopic origin of the barrier which is formed at intimate metal-semiconductor contacts is currently an unresolved and controversial issue.[1-5] Although many recent experimental studies[5] have suggested the occurrence of a wide range of chemical and physical phenomena at these contacts, no direct connections between these various interfacial phenomena and the observed Schottky barriers have been established. To address such a complex question sensibly, it is necessary to consider some well-characterized and simple limiting cases. To this end, an extensive experimental investigation of the electronic and electrical properties of Al chemisorbed on the (110) surface of GaAs has recently been carried out.[6,7] In this Letter we show, for the first time, that the chemistry and structural relaxation associated with the chemisorption of Al on GaAs *completely* determines the barrier experimentally observed at submonolayer coverage. We find that two principal features of the chemisorption process determine the induced surface: Chemisorbed Al replaces the surface Ga and the displaced Ga caps the surface As. This is in agreement with the results of recent chemical-shift studies.[6-7] This displacement reaction involves a charge transfer from the Al to the surface Ga which determines the surface dipole. Second, the chemisorption of the metal induces a unique surface relaxation which is uncharacteristic of the clean surface and is responsible for the observed band bending at submonolayer coverage. The total change in the work function, which is the sum of the induced band bending and the induced surface dipole, is thus completely determined by the electronic structure of this new chemisorption complex.

In this Letter we will first briefly summarize the major recent experimental findings concerning this system. Second, we will present theoretical valence-band densities of states, calculated for several chemisorption geometries, which indicate that Al displaces Ga at the surface. Third, we will show that the observed band bending at submonolayer coverage is due to a new structural relaxation which is induced by chemisorption of the metal.

Experimental data for a submonolayer coverage of Al deposited on n-GaAs provide several principal results. To summarize, the 1×1 low-energy electron-diffraction pattern persists,[7] indicating that the translational symmetry of the clean surface is not perturbed. Photoemission from the core states shows that the chemisorbed Al $2p$ state is chemically shifted by 0.7 eV to increased binding energy with respect to the $2p$ state in Al metal, and the binding energy of the surface Ga $3d$ core state is decreased 0.95 eV by exposure to Al.[6,7] This indicates that the surface Ga atoms gain charge, with the chemisorbed Al losing charge at the surface. The GaAs surface work function increases by 0.45 eV after adsorption of a half-monolayer of Al, with approximately 0.2 eV of this increase attributable to band bending as determined by a surface photovoltage technique.[7] The additional increase is attributed to a negative surface dipole which provides a 0.25-eV discontinuity in the electrostatic potential across the interface. Furthermore, photoemission studies of the GaAs valence bands before and after Al exposure show changes in several key features which are attributable to changes in the electronic structure of the surface layer.[6] These changes are shown in Fig. 1. The spectrum of the clean material shows three principal peaks labeled a, b, and c which correspond, respectively, to emission from As-$4s$-derived states, Ga-$4s$-As-$4p$-derived states, and As-$4p$-derived

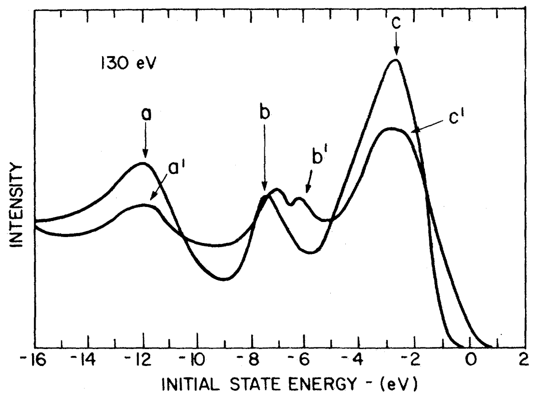

FIG. 1. Experimental photoemission spectra from Ref. 6 for clean GaAs(110), and GaAs(110) after deposition of ~ 1 monolayer of Al. The principal photoemission features of the clean and exposed surfaces are denoted by the unprimed and primed labels, respectively. (The valence-band maximum occurs at ≈ – 1 eV.)

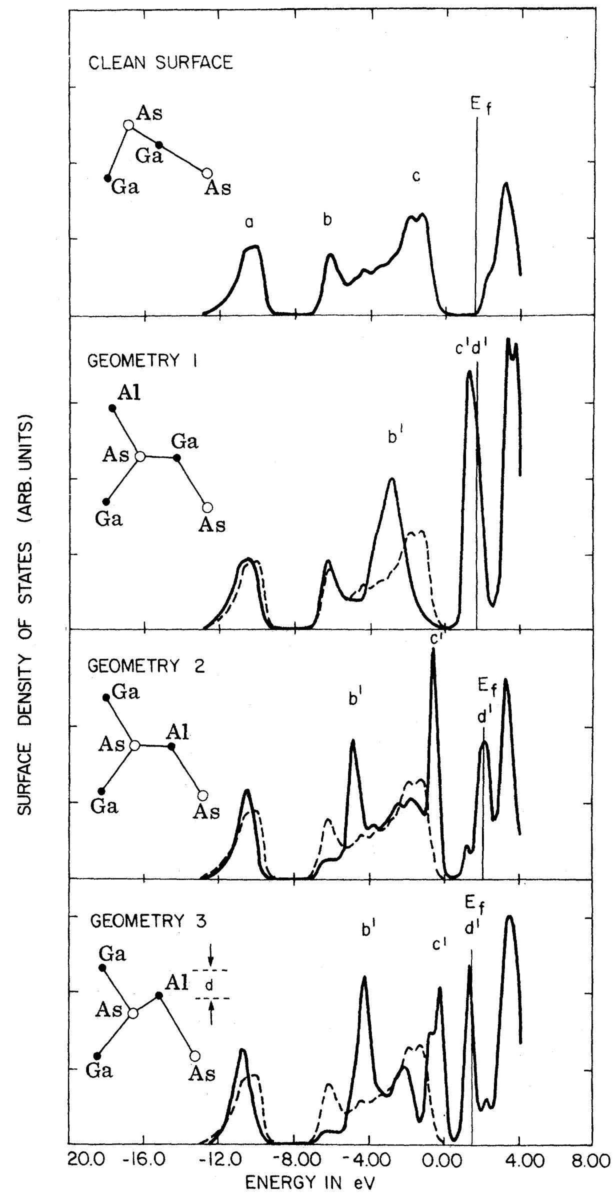

FIG. 2. Theoretical densities of states for clean relaxed GaAs(110) (top panel) and for Al chemisorbed on GaAs(110) in three different configurations shown in the insets. In all cases the valence-band maximum occurs at 0.0 eV. The dashed lines in the lower traces represent the clean spectrum for comparison. E_F defines the Fermi energy for an n-type sample for each configuration.

states. As Al is chemisorbed a new feature appears near – 6 eV (the valence-band maximum occurs $\lesssim -1.0$ eV in this spectrum), the peak labeled c broadens, and new states occur in the bandgap ($E \gtrsim -1.0$ eV).

To model this system theoretically, we have applied an empirical tight-binding model to the GaAs(100) surface,[8,9] using an effective-field technique discussed in detail elsewhere.[9] The empirical parameters describing the GaAs and AlAs bonds are obtained by fitting critical points from a bulk-sensitive photoemission experiment[10] and from a self-consistent orthogonalized-plane-wave calculation,[11] respectively. In the process of fitting these parameters, we observe that the diagonal matrix element representing the "self-energy" of the Al 3s state tends to lie significantly higher (1.8 eV) than that of the Ga 4s state. This result reflects a similar trend in the isolated atoms, for which a Hartree-Fock-Slater calculation yields a difference of 1.27 eV.[12]

This relative shift of the cation valence s levels is the most significant difference between the AlAs and GaAs models, and provides a means with which to identify the coordination of these species on the surface. This analysis is demonstrated in Fig. 2. In the figure, we show surface densities of states for clean relaxed GaAs(110) and for Al chemisorbed on GaAs(110) in three distinct geometries, shown in the insets. For the clean surface, shown in the top panel, we identify the peaks labeled a, b, and c with the three prominent features observed in the photoemission data of Fig. 1. However, since only 20–30% of the experimental photoyield is surface derived, we are merely interested in the strong metal-induced surface features in the theory which give rise to the observed changes in the experimental traces after Al exposure. Consider theoretical geometries 1 and 2 which differ merely by having the Al and Ga interchanged on the surface. The surface is assumed to be unrelaxed in both cases, with the additional metal atom capping the surface As as though the lattice were continued. In geometry 1, in which Al is the singly coordinated species, we obtain a prominent feature labeled b' occurring roughly 3.5 eV above the feature labeled b in the clean spectrum. These states are strongly localized on the $3s$ orbitals of the singly coordinated Al. The analogous states which are localized on the Ga s orbitals when the Ga is the singly coordinated capping species occur only 1.5 eV above the peak labeled b in the top panel. Further calculations show that the locations of these states labeled b' are relatively insensitive to relaxations of the substrate surface layer. Therefore, the location of these states is principally determined by which species is singly coordinated at the surface. The photoemission data of Fig. 1 clearly show that Al chemisorption induces states within 2 eV of the clean spectral feature labeled b. Therefore, we conclude that the Ga is the singly coordinated species at the surface, with the Al multiply (most probably threefold) coordinated.

This exchange reaction immediately explains the origin of the induced surface dipole. We have calculated the electronic structure of surfaces exhibiting this exchange reaction in the unrelaxed and in various relaxed geometries. In *all* of these cases a charge transfer from $0.1e$ to $0.2e$ occurs from the threefold-coordinated Al to the singly coordinated Ga. This result is thus consistent with the relative charge states inferred from the core-level photoemission measurements,[6,7] and *in addition* it predicts a negative surface dipole, in agreement with the experimental observation. It is important to note that the chemical-shift studies are consistent with the sign of the observed surface dipole only if the Ga atoms are further from the bulk than the chemisorbed Al.

For a half-monolayer of Al chemisorbed on a 1×1 GaAs surface, there are an odd number of electrons in each surface unit cell, and thus the surface is "metallic" with the Fermi energy determined by a partially filled surface band. In geometry 2 the partially filled band is a threefold-coordinated Al dangling-bond band, d', which is centered 0.4 eV *above* the conduction-band edge. Thus model 2 predicts that the bands will bend downward by 0.4 eV at the surface of an n-type sample, in conflict with the upward 0.2-eV band bending found experimentally.

However, note that the presence of *intrinsic* charge in cation-derived dangling-bond states is a feature which is very uncharacteristic of the clean semiconductor surface. At the clean surface, the analogous states (a Ga dangling bond) is empty and is pushed into the conduction band by a relaxation in which the surface Ga shifts towards the bulk.[13] The presence of charge in the cation dangling-bond orbital at the metallic surface, as in geometry 2, prevents such a relaxation, since pushing these electrons further into the conduction band requires additional surface electronic energy. In fact, after chemisorption of Al the 1×1 surface can lower its energy by relaxing such that the threefold-coordinated Al moves *away* from the bulk as in geometry 3. Integrating the valence-band spectrum shown for this new geometry, we find that the surface electronic energy is lowered by 0.3 eV per unit cell by allowing the threefold-coordinated atom to rotate away from the bulk, reducing the As-Al-As bond angle to 94°. Although bond lengths are slightly distorted in this particular geometry,[14] we find a similar energy reduction in "counterrelaxed" geometries in which all bond lengths are held fixed. Thus after the chemisorption of Al, the surface energy is lowered in a counterrelaxed configuration.

This surface counterrelaxation not only lowers the surface energy but also explains the experimentally observed band bending. As shown in the lowest panel of Fig. 2, the Fermi energy which is determined at the surface by the partially filled band, d', falls 0.15 eV below the conduction-band edge. This agrees very well with the 0.2-eV band bending measured experimentally.

In addition, this particular geometry is also consistent with *all* of the previously mentioned experimental data. The partially filled band at the Fermi energy is responsible for the observed photoyield from states in the bandgap $(-1.0 \leq E \leq 0.0)$ in Fig. 1. The states labeled c' in geometry 3 of Fig. 2 are associated with the apparent broadening of the peak c into c' in the photoemission spectrum, and the theoretical peak labeled b' is associated with the presence of a singly coordinated Ga at the surface as noted previously. Geometry 3 predicts a charge transfer of $0.15e^-$ from the chemisorbed Al to the surface Ga, in agreement with the relative charge states inferred from the core-level photoemission. Moreover, if we take the distance from the Al to the surface Ga measured along the surface normal as the effective dipole width (shown as d in Fig. 2), and screen the surface electrostatic potential with an appropriate q-dependent dielectric function,[15] we obtain a surface dipole potential of 0.2 eV, in remarkably good agreement with the 0.25-eV potential inferred experimentally.[16] We emphasize that the electronic structure of the counterrelaxed configuration of Fig. 2 is in good agreement with both the core-state and valence-state spectroscopic studies of this system and the observed electrical properties of the exposed surface. Thus the surface barrier induced by chemisorption of a half-monolayer of Al on GaAs is completely determined by the electronic structure of a simple Al-As-Ga chemisorption complex. Note that this relaxation should not be peculiar to Al-GaAs and may be expected for the chemisorption of many group-III metals on III-V-compound substrates.

Finally, we should emphasize that while we are gaining a better understanding of the influence of a submonolayer coverage of metal on a semiconductor substrate like GaAs, the physics at higher coverages seems to be significantly more complicated. Several workers have observed the diffusion of Ga away from the interface as the deposited Al thickness increases,[7] and similar phenomena have been suggested at other interfaces.[17] Since the interfacial chemistry is likely to be changing significantly in this limit, a microscopic understanding of the Schottky barrier ultimately formed at contacts will await a more complete treatment of these interface bonds.

It is a pleasure to acknowledge helpful discussions with D. J. Chadi and L. J. Brillson. One of us (J.D.J.) acknowledges partial support from Joint Services Electronics Program Contract No. DAAG-29-78-C-0020 and the Alfred P. Sloan Foundation.

[1] S. Kurtin, T. C. McGill, and C. A. Mead, Phys. Rev. Lett. 22, 1433 (1970).

[2] S. G. Louie and M. L. Cohen, Phys. Rev. Lett. 35, 866 (1975).

[3] L. J. Brillson, Phys. Rev. Lett. 38, 2451 (1977), and 40, 260 (1978).

[4] J. R. Chelikowsky, Phys. Rev. B 16, 3618 (1977).

[5] See, for instance, J. Vac. Sci. Technol. 15, 1317ff (1978), and references therein.

[6] R. Z. Bachrach, R. S. Bauer, and J. C. McMenamin, in *Proceedings of the Fourteenth International Conference on the Physics of Semiconductors*, edited by R. A. Stradling (Plessy, Edinburgh, 1978).

[7] L. J. Brillson, R. S. Bauer, R. Z. Bachrach, and J. C. McMenamin, to be published.

[8] D. J. Chadi, Phys. Rev. B 18, 1800 (1978).

[9] E. J. Mele and J. D. Joannopoulos, Phys. Rev. B 17, 1816 (1978).

[10] L. Ley, R. A. Pollak, F. R. McFeely, S. P. Kowalczyk, and D. A. Shirley, Phys. Rev. B 9, 600 (1974).

[11] F. Herman, R. L. Kortum, I. B. Ortenburger, and J. P. Van Dyke, Aerospace Research Laboratory Report No. ARL69-0080, 1969 (unpublished), Sect. 21.

[12] F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice Hall, Englewood, Cliffs, N. J., 1963).

[13] A. R. Lubinsky, C. B. Duke, B. W. Lee, and P. Mark, Phys. Rev. Lett. 36, 1058 (1976).

[14] An empirical model to quantitatively include bond-length changes in a surface total-energy calculation has recently been suggested by D. J. Chadi, Phys. Rev. Lett. 41, 1062 (1978).

[15] J. P. Walter and M. L. Cohen, Phys. Rev. B 2, 1821 (1970).

[16] Since the empirical tight-binding method used in this calculation is essentially an energy-band interpolation method, we assign physical significance only to the direction of charge transfer obtained in this problem. Nonetheless, the quantitative accuracy of this calculation of the surface dipole is gratifying.

[17] I. Lindau, P. W. Chye, C. M. Garner, P. Pianetta, C. Y. Su, and W. E. Spicer J. Vac. Sci. Technol. 15, 1332 (1978).