

Electronic States of Metal Atoms on the GaAs(110) Surface Studied by Scanning Tunneling Microscopy

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Using the scanning tunneling microscope, Au adsorbates are found to bond to Ga atoms on the GaAs(110) surface. A characteristic spectrum of band-gap states is observed for the Au adsorbates. Both donor and acceptor states are seen, and they are identified with the first and second electron states of the Au–Ga bond, respectively.

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The mechanism of Schottky-barrier formation at metal-semiconductor interfaces has been studied for decades.¹ This problem is particularly interesting on the GaAs(110) surface, in which relaxation or “buckling” of the clean surface sweeps the dangling-bond-related surface states out of the band-gap region.^{2,3} Deposition of metal onto the surface then “pins” the surface Fermi level near midgap, implying the presence of states located within the band gap.⁴ These band-gap states are somehow induced by the metal adsorbates, but the character of the states remains unknown. In a recent scanning tunneling microscope (STM) study, the spectrum of these states was observed for Sb adsorbates on the GaAs(110) surface.⁵ However, the fundamental nature of those states, i.e., their precise distribution in real space, was not identified due to various limitations in the experimental procedure.

In this work, we use the STM to study the geometric structure and electronic states of Au atoms on the GaAs(110) surface. Isolated atoms, and small clusters of atoms, are found on the surface. We find that the Au adsorbates bond to surface Ga atoms. The spectrum of states for the adsorbates is observed to consist of an acceptor state located in the upper part of the band gap and a donor state resonant with the valence band. We find that the maximum of the state density for both the donor and acceptor states is located directly on top of the Au atoms. A model is proposed in which these states constitute the first and second electron levels of the Au–Ga bond, respectively. Tails of these adsorbate-induced states are weakly observed, extending away from the adsorbate and having local maxima located at the position of neighboring surface Ga atoms.

The experimental techniques used in this study have all been previously described,^{5,6} with two exceptions. First, we found in our previous studies that the observation of band-gap states on GaAs(110) was hampered by limited surface conductivity (on the clean surface there are no states within the band gap to provide a conduction channel).² We have overcome this problem by using very highly doped GaAs; Zn diffusions are performed at 1000°C for 4 h, producing doping concentrations⁷ of

about 10^{20} cm^{-3} . The samples are then cleaved in ultrahigh vacuum ($P < 4 \times 10^{-11}$ Torr). Au is deposited using a filament evaporator, and the coverage is monitored with a crystal-thickness monitor. STM images are acquired at a constant current of 0.1 nA. The second technical advance made in this work concerns the acquisition of constant-current STM images for states within the band gap. To permit imaging within the band gap, we use the interrupted feedback method,⁶ in the imaging mode.⁸ To achieve a large dynamic range, current images are acquired at many tip-sample separations (26 values of the separation over a range of 4 Å were used for the data presented here). This data set is subsequently searched for the tip-sample separations needed to produce some constant value of the tunnel current. The image thus obtained is identical to a conventional constant-current image, with the exception that a lower limit exists on the tip-sample separation, thus preventing contact between tip and sample.

In Fig. 1 we show an STM image of the GaAs(110)

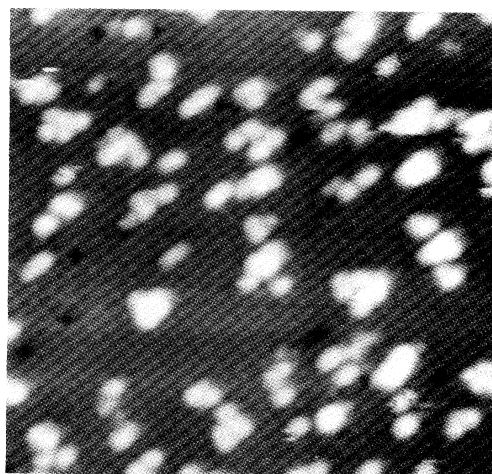


FIG. 1. $220 \times 220 \text{ \AA}^2$ STM image of gold on the GaAs(110) surface, acquired with a sample voltage of -2.5 V . The Au coverage is 0.1 ML. The topographic height is displayed by a grey scale, ranging from 0 (black) to 4 Å (white).

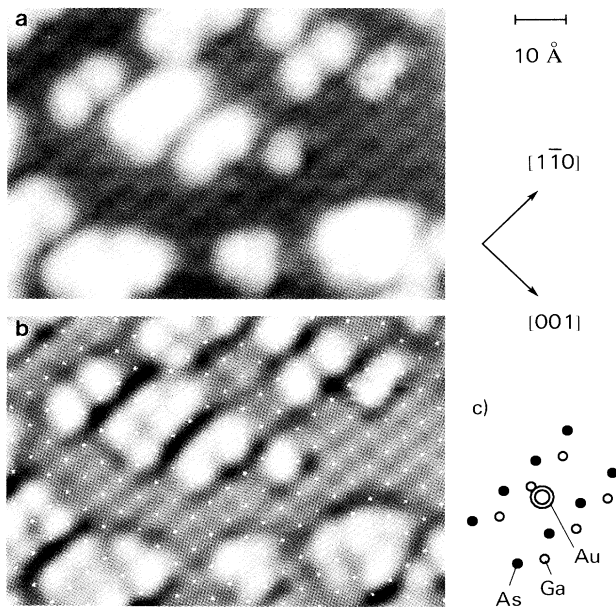


FIG. 2. $90 \times 60 \text{ \AA}^2$ STM images of 0.25-ML Au on the GaAs(110) surface, acquired with a sample voltage of -2.5 V . The grey scale corresponds to (a) surface height, and (b) surface curvature. A top view of the atomic positions is pictured in (c), with a $2.2 \times$ expanded lateral scale.

surface covered with 0.1 ML of gold [1 ML (monolayer) $= 8.85 \times 10^{14}$ atoms/cm 2]. Small clusters of Au atoms are seen as surface protrusions, typically 2 \AA high. Some of the protrusions appear to be localized within a single surface unit cell, and we believe that these features are individual Au atoms. Figure 2 shows images from another sample, covered in this case with 0.25 ML of gold. The grey scale of Fig. 2(a) corresponds to surface height, and the contrast is enhanced in Fig. 2(b) by plotting the curvature of the surface.⁹ A grid of points is overlaid on Fig. 2(b), located at the maxima of the corrugation on the clean GaAs surface. For the tunneling voltage used, -2.5 V on the sample relative to the tip, these maxima correspond to the location of the As atoms on the surface.¹⁰ In Fig. 2(b) we see that the location of the Au atoms is roughly equidistant between four As atoms, thus placing the Au atom $\sim 1.4 \text{ \AA}$ laterally away from a surface Ga atom. This binding site of the Au atoms, pictured in Fig. 2(c), indicates that the Au atoms bond to Ga atoms. We note that, along the $[1\bar{1}0]$ direction, the Au atoms usually occupy every *second* unit cell on the surface.

We have performed spectroscopic measurements on the Au atoms and clusters, an example of which is shown in Fig. 3. The image of Fig. 3 was acquired from the same surface region as that of Fig. 2 (as can be verified by a comparison of the images), although Fig. 3 displays somewhat lower resolution presumably due to a blunter probe tip. In the image of Fig. 3 we mark the locations

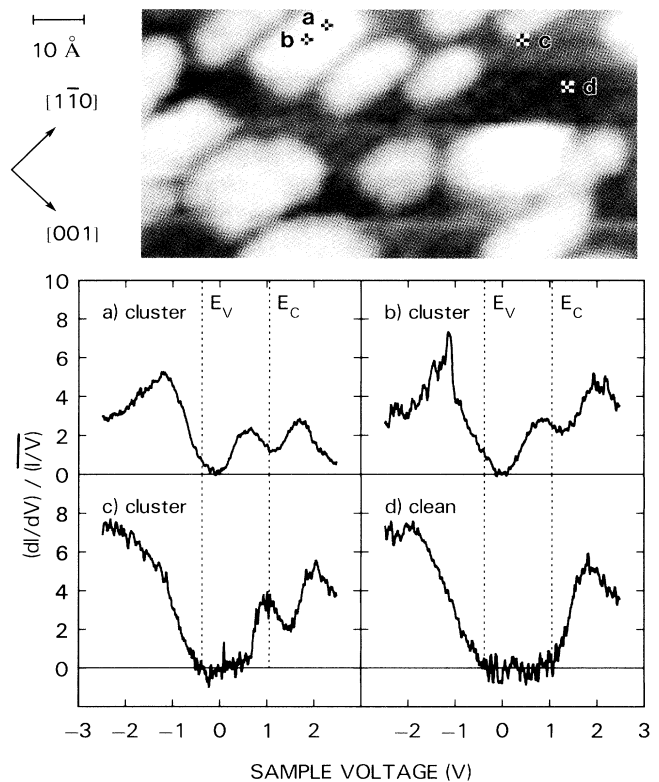


FIG. 3. Normalized conductivity vs voltage, measured on and off the Au clusters. The $100 \times 55 \text{ \AA}^2$ STM image of the surface is shown in the top part of the figure, acquired at -2.5 V . Checkered markers give the locations at which the spectra were acquired.

a-d where tunneling spectra were acquired, and those spectra are shown in the lower part of the figure. We plot the conductivity dI/dV , acquired and normalized as previously described.⁵ The sample voltage (*x* axis) corresponds to the energy of a state relative to the surface Fermi level. On the clean GaAs surface, spectrum *d*, we observe a band-gap region with width of 1.4 eV . The edges of this region are marked E_V and E_C , denoting the valence-band maximum and conduction-band minimum, respectively. In spectra *a-c*, located on the Au clusters, we observe a state within the upper part of the band gap. We also observe an increase in spectral intensity in the valence band, seen most clearly in spectra *a* and *b*. Such features are reproducibly observed on almost all the Au clusters, although the gap state is easier to discern than the valence-band resonance since, in the gap, there is no overlapping contribution from the clean surface. The intensity of the spectral features varies from cluster to cluster, although their energy locations are roughly constant. We find that the gap state is located near $E_V + 1.0 \text{ eV}$, and the valence-band resonance occurs roughly at $E_V - 0.7 \text{ eV}$. Both states form bands, with widths in the range $0.5\text{--}1.0 \text{ eV}$. Significant tailing of the

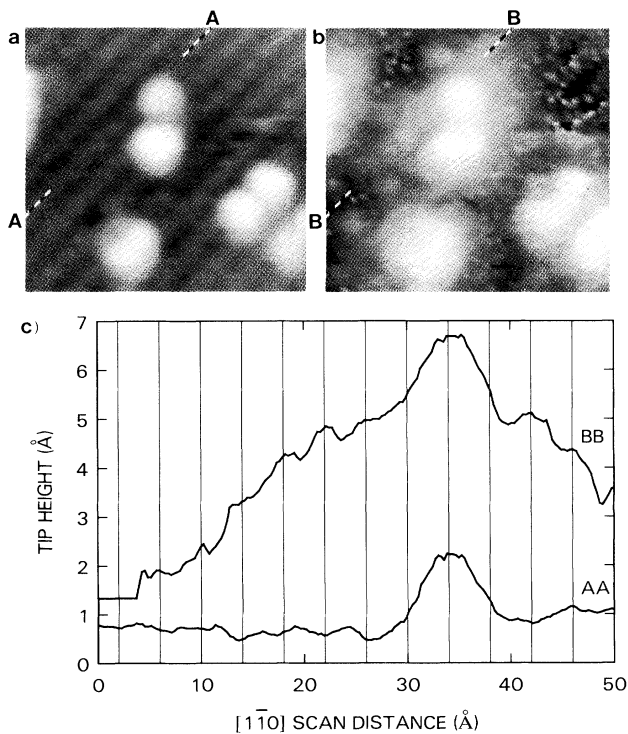


FIG. 4. $50 \times 50 \text{ \AA}^2$ STM images of 0.1-ML Au on the GaAs(110) surface. Images were acquired simultaneously at sample voltages of (a) -2 and (b) $+1$ V. Cross sections of the images are shown in (c) (the zero of tip height is arbitrary). Thin vertical lines in (c) denote the positions of Ga atoms on the surface.

valence-band resonance occurs into the lower part of the band gap.

The spectrum of states observed here for Au is very similar to that previously found for Sb and Bi adsorbates on GaAs(110).^{5,11} In general, empty states observed in tunneling spectra have acceptor character ($-/0$ charge states), and filled states have donor character ($0/+$ charge states). This general behavior is true whenever the concentration of surface states exceeds the bulk space charge of 10^{12} – 10^{13} cm^{-2} , which is satisfied in our experiments for which the surface state density is greater than $0.1 \text{ ML} \approx 10^{14} \text{ cm}^{-2}$. Thus, the band-gap states observed here are acceptors, and the valence-band resonances are donors.

We have further explored the nature of the adsorbate-induced states by spatially imaging the state density. The results are shown in Fig. 4. In Fig. 4(a) we show an STM image, acquired at -2 V, from a surface covered with 0.1 ML of Au. Two Au atoms are visible near the center of the image. In Fig. 4(b) we show exactly the same surface region, imaged at a sample voltage of $+1$ V, corresponding to an energy located near the top of the band-gap region. We find that the maxima in the state density seen for both the filled (donor) and the empty

(acceptor) states are spatially coincident, located at a site which, in Fig. 2, we crudely associated with the position of the Au atom itself. Given that the Au adsorbates bond to Ga atoms, a simple model can be developed for the identification of the states. A hybrid orbital is formed between the Au $6s$ level and the Ga sp^3 dangling bond. Au has one electron to donate to this level, thus forming a *filled* state. We associate that state with the spectral features observed in the valence band. The Au-Ga hybrid orbital can accommodate a second electron in an *empty* state, which will be higher in energy than the filled state by the intra-atomic Coulomb repulsion of the electrons U .¹² We associate this empty level with the state observed in the upper part of the band gap. Qualitatively, this description of the bonding states is consistent with some recent theoretical works on metal adsorbates,^{12,13} although we feel that more detailed calculations are necessary to fully understand the bonding states for this system.

In addition to the Au-Ga bonds, the states seen in Fig. 4(b) also display weak tails extending away from the adsorbates. To permit a detailed examination of these wave-function tails, we show in Fig. 4(c) cross sections of these wave-function tails. The cross sections are taken along the lines *AA* and *BB* marked in Figs. 4(a) and (b), respectively. Cross section *AA* shows a maximum for the Au atom, and the periodic corrugation of the clean surface. Cross section *BB* also shows a maximum on the Au atom, but then falls off continuously as the lateral distance from the adsorbate increases. Note that the cross sections in Fig. 4 are chosen to emphasize the tails of the state density around the Au adsorbates, thus passing through the side of an adsorbate. In cross section *BB*, we observe small maxima on either side of the Au adsorbate. Vertical lines in Fig. 4(c) are drawn through the *minima* of the surface corrugation in *AA*, and these vertical lines pass through the *maxima* seen in *BB*. For the negative voltage of Fig. 4(a), the maxima in *AA* correspond to the position of As dangling bonds,¹⁰ and thus the maxima seen in *BB* are localized at the position of Ga dangling bonds. Broadening of the cross sections due to the finite size of the probe tip could contribute to these apparent tails of the states, although the observation of distinct corrugation localized on the Ga atoms provides strong evidence that this is not entirely a probe-tip effect. We find that the tails of the wave function involve neighboring Ga dangling bonds, pulled down in energy from the conduction band. This observation is consistent with “unbuckling” of the surface around the adsorbates, although other mechanisms may equally well produce these wave-function tails.

The consistency of the results reported here for Au with those discussed elsewhere for Sb and Bi adsorbates^{5,11} leads us to conclude that the nature of the band-gap states deduced here is similar for many metal systems on GaAs(110). In our model for Au-Ga, the

metal-semiconductor bonds produce the band-gap states. For Sb and Bi adsorbates, the metal adsorbates form ordered monolayers on the surface which themselves have a band gap in their spectrum of states, and states within this band gap were observed to exist at the edge of monolayer terraces. One common feature in all of these systems seems to be the occurrence of *partially occupied bonds* which produce states within the band gap. These bonds consist of hybrids of the metal orbitals and the GaAs surface dangling bonds. Complete saturation of the bonds (e.g., as occurs for a monolayer of Sb) leads to a band gap in the energy spectrum and a surface Fermi level which is free to move within this band gap. However, partial occupation of the bonds, as occurs for Au adsorbates or at the edge of Sb or Bi islands, produces states in the band gap which pin the Fermi level. Additional types of defects, such as antisites, are apparently not needed to produce the Fermi-level pinning at the surface.⁴ Also, the complete formation of a metal overlayer is not required to produce the states observed here. The band-gap states we observe arise purely from the properties of the metal-semiconductor bonds, and these hybrid states provide the mechanism for Fermi-level pinning at the surface.

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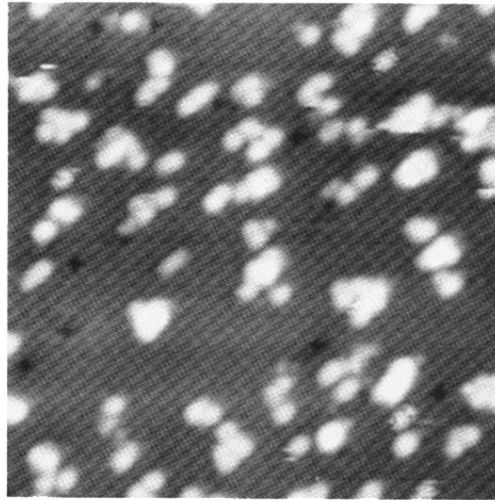


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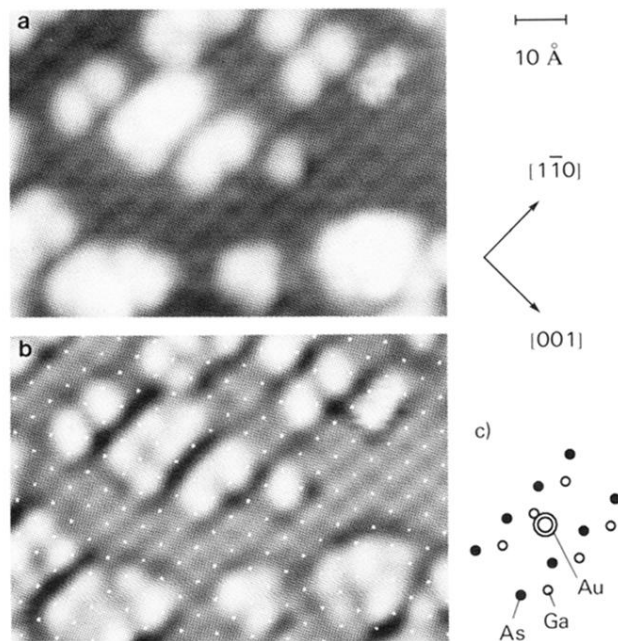


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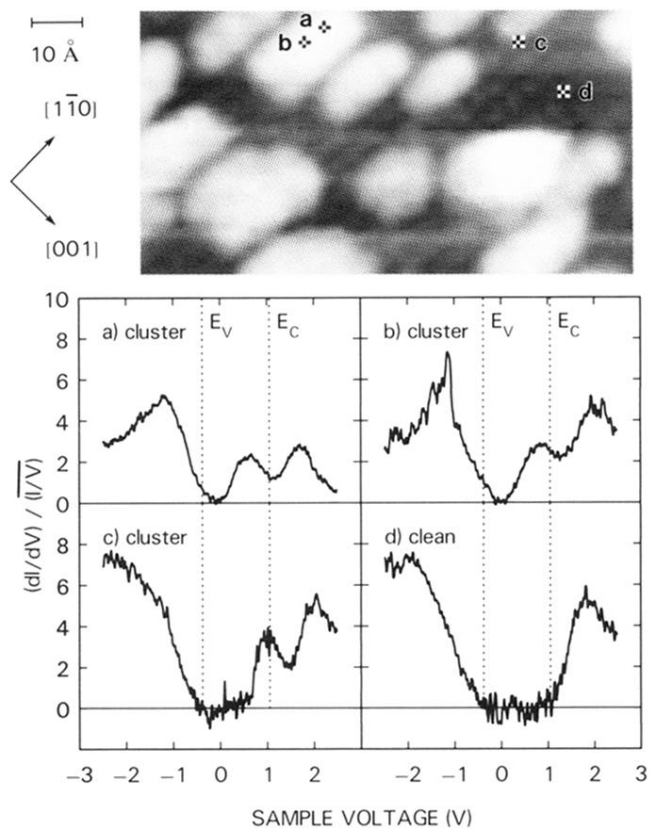


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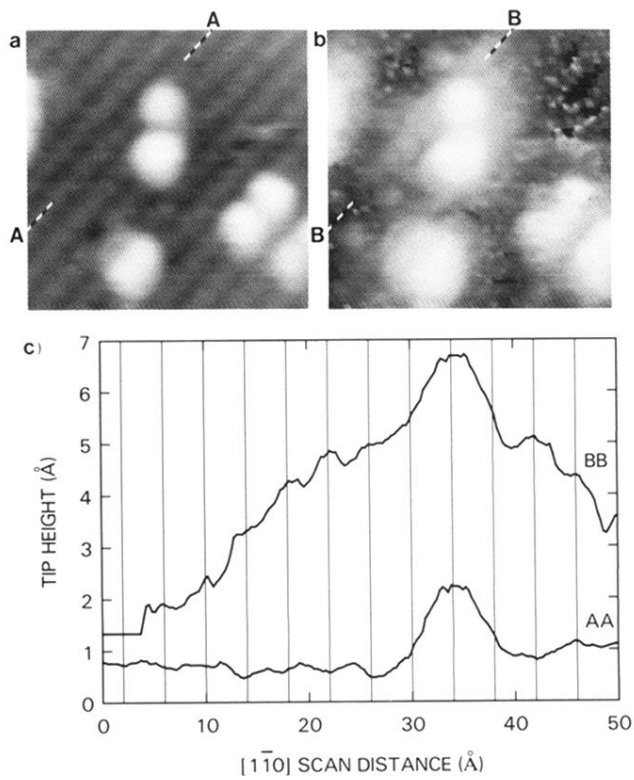


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