

## Two-dimensional band structure of chemisorbed chlorine on GaAs (110)

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The two-dimensional electronic energy bands of an ordered Cl overlayer on GaAs (110) were mapped by angle-resolved photoemission spectroscopy with synchrotron radiation. The results were compared to bands calculated with an empirical tight-binding approach. This comparison shows that the Cl adatoms are bound to As atoms and that the substrate atoms are relaxed from their positions in a way qualitatively similar to that of clean-surface GaAs (110).

### I. INTRODUCTION

We have investigated the two-dimensional energy-wave-vector dispersion curves of an ordered chemisorbed monolayer of Cl atoms on the (110) face of GaAs. The study involved experimental mapping of the dispersion curves by angle-resolved photoemission spectroscopy with synchrotron radiation<sup>1-5</sup> These experimental dispersion curves were theoretically analyzed by an empirical tight-binding band-structure calculation.<sup>6-7</sup> Our results provide further evidence for a chemisorption model in which the Cl atoms are bound to the As substrate atoms rather than to the Ga substrate atoms.<sup>6</sup> We also found increasing evidence that the substrate atoms close to the surface are displaced from their bulk positions, similar to what happens for the clean GaAs (110) surface.<sup>8</sup>

Chemisorbed atomic chlorine on semiconductor surfaces was recently used by several authors for prototypical photoemission studies of chemisorption geometries.<sup>5,6,9,10</sup> In particular, we extensively investigated<sup>6</sup> the chemisorption of Cl atoms on III-V surfaces by angle-integrated photoemission spectroscopy and by theoretical calculations of the local density of states. The experimental position of the photoemission spectral peaks was then used to investigate the correct chemisorption site. For all the III-V surfaces under investigation we found evidence<sup>6</sup> that the Cl adatoms are bound to the anion atoms of the substrate. In the present investigation we have studied the band structure of GaAs (110) + Cl by angle-resolved photoemission spectroscopy<sup>1-5</sup> and by further tight-binding calculations. The energy-wave-vector dispersion curves were experimentally mapped along the  $\bar{\Gamma}\bar{X}$  and  $\bar{\Gamma}\bar{X}'$  high-sym-

metry lines of the two-dimensional Brillouin zone (i.e., the [110] and [001] directions, respectively). The best agreement between theory and experiment is found for a relaxed configuration of the first substrate atoms qualitatively similar to that of the clean GaAs (110) surface.<sup>8</sup> Several features in the experimental band structure show that the interface relaxation suggested in Ref. 6 is qualitatively correct. The magnitude of this relaxation is probably smaller than that for the clean (110) surface of GaAs.<sup>8</sup>

Section II of this article will outline the experimental procedure for band-structure mapping. The energy-wave-vector dispersion curves given by this technique will be compared in Sec. III to the theoretical results and our conclusions will be summarized in Sec. IV.

### II. EXPERIMENTAL BAND-STRUCTURE MAPPING

The experimental band-structure mapping by angle-resolved photoemission spectroscopy, introduced by Smith and Traum,<sup>1</sup> has already been discussed in the recent literature<sup>1-5</sup> and we present here a brief summary of our experimental procedure. In an angle-resolved photoemission experiment the wave-vector component parallel to the surface,  $k_{\parallel}$ , is conserved. Therefore  $k_{\parallel}$ , for an electronic state at an initial energy  $E$ , is simply given by

$$[2m(E + \hbar\omega - \Delta)]^{1/2} \sin\theta/\hbar.$$

Here  $E$  is referred to a given origin, e.g., the top of the valence band  $E_v$ , and  $\Delta$  is the position of the vacuum level with respect to this origin. Peak positions in the energy distribution curve (EDC) taken for different values of the polar angle  $\theta$ , therefore, give a plot of  $E$  as a function of  $k_{\parallel}$ , i.e., a two-dimensional projection of the band

structure provided matrix-element effects and other final-state corrections are not strongly dependent on energy or wave vector. For nearly-two-dimensional systems such as layer compounds and chemisorbed overlayers,<sup>1,2,5</sup> this projection coincides in first approximation with the entire band structure.

In our experiments we measured angle-resolved EDC's by means of a vidicon-camera parallel detection system.<sup>11</sup> The system consisted of a retarding-grid energy analyzer, a channel-plate electron multiplier, a fluorescent screen, and a minicomputer-controlled vidicon camera for fast parallel acquisition of many EDC's in different directions. In the present experiments the angular resolution was better than  $\pm 1.5^\circ$  and the energy resolution better than 300 meV. Further details on the experimental system can be found in Ref. 11. The EDC's were taken on cleaved GaAs (110) surfaces with monolayer atomic-chlorine coverage. The surfaces cleaved *in situ* were immediately exposed to a Cl atmosphere following the procedure described in Ref. 6. Low-energy electron diffraction experiments done in a separate experimental chamber show that Cl chemisorbs on GaAs (110) in an ordered  $1 \times 1$  overlayer. Two different photon energies were used in the experiments— $\hbar\omega = 19$  and 25 eV. These photons were obtained from the broad spectral output of the storage ring Tantalus at the University of Wisconsin Synchrotron Radiation Center upon filtering by a vertical Seya-Namioka monochromator.

Figure 1 shows a number of angle-resolved EDC's taken at  $\hbar\omega = 25$  eV for different directions of collection. The azimuthal angle  $\phi$  was selec-

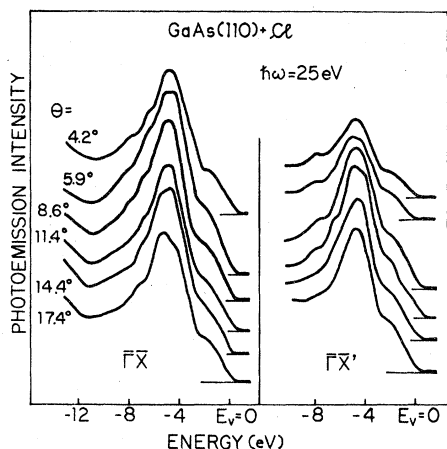


FIG. 1. Angle-resolved energy distribution curves (EDC's) along two high-symmetry directions of the two-dimensional Brillouin zone. The EDC's were taken at a photon energy of 25 eV and for several different values of the polar angle  $\theta$ .

ted to coincide with either the  $\overline{\Gamma X}$  direction or the  $\overline{\Gamma X'}$  direction of the two-dimensional Brillouin zone. The analysis of the EDC's reveals five different spectral features whose positions in energy depend on  $\hbar\omega$  and on the direction of collection. Figure 2 shows the energy versus  $k_{||}$  points deduced from all the EDC's taken at  $\hbar\omega = 19$  and 25 eV. These points are plotted along the above-high-symmetry directions,  $\overline{\Gamma X}$  and  $\overline{\Gamma X'}$ . Notice in particular that the experiment plots are reasonably symmetric around the zone-center  $\overline{\Gamma}$  points in the extended-zone scheme as expected for the correct  $E$  versus  $k_{||}$  dispersion.

### III. THEORETICAL INTERPRETATION OF THE EXPERIMENTAL BAND STRUCTURE

The band structure of GaAs (110) + Cl was calculated for three different chemisorption models using an empirical tight-binding scheme.<sup>6,7</sup> In model A the chlorine atoms are bound to surface arsenic atoms and both Ga and As substrate atoms close to the surface are displaced from their bulk position. The relaxed substrate-atom positions were chosen to coincide with those of the clean reconstructed GaAs (110) surface, i.e., the anions are displaced outwards and the cations inwards with respect to the unrelaxed configuration.<sup>8</sup> In model B the chlorine atoms are also bound to the arsenic atoms but Ga and As sub-

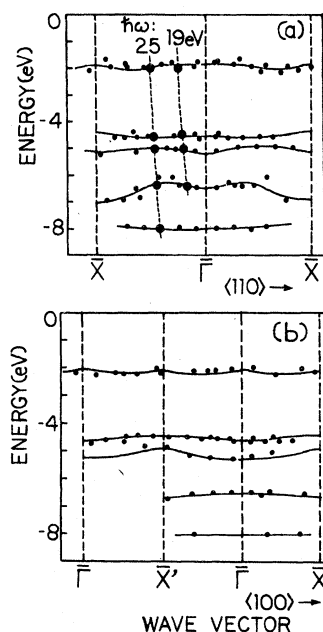


FIG. 2. (a) Experimental plot of the GaAs (110) + Cl band structure along the  $\overline{\Gamma X}$  direction (i.e., the  $[1\overline{1}0]$  direction). (b) Along the  $\overline{\Gamma X'}$  direction (i.e., the  $[001]$  direction). The two dashed lines show portions of the parabolic relationship  $k_{||} \propto \sqrt{E} \sin \theta$ .

strate atoms are in their bulk positions. In model *C* the chlorine atoms are bound to the gallium atoms with the substrate atoms still in their bulk positions. We obtained a negative charge transfer from substrate to adatoms of 0.24, 0.22, and 0.32 electrons per atom for models *A*, *B*, and *C*. The extra negative charge transferred to each adatom in model *C* pushes up the chlorine  $3p$  states to lower binding energies. The resulting position in energy of these states is in poor agreement with the earlier angle-integrated photoemission results<sup>6</sup> and with our present angle-resolved data. Therefore we rule out model *C* and concentrate our attention on models *A* and *B*, which give a position in energy of the  $p$  electrons in good agreement with the experimental data.

The calculated two-dimensional GaAs (110) + Cl bands for model *A* are shown in Fig. 3 (dashed lines) along the high-symmetry directions of the Brillouin zone. The shaded area corresponds to the projection of the three-dimensional band structure of bulk GaAs. Superimposed on the theoretical energy bands are the experimental bands from Fig. 2 (shown as solid lines). In most cases the interpretation of the experimental bands is fairly straightforward. For example, the shallowest energy experimental band corresponds to the theoretical band *g* along the  $\bar{\Gamma}\bar{X}$  line and to the theoretical band *g'* along the  $\bar{\Gamma}\bar{X}'$  line. Band *g* is a substrate resonance with an ~30 percent contribution of Cl  $3p_x p_y$  states, while band *g'* is almost entirely due to the GaAs substrate and it is also present on the clean GaAs (110) surface. The deepest energy experimental

band clearly corresponds to the theoretical band *b*, which is due to Cl  $3p_z$  states and to As "dangling-bound"  $p_z$  states (with minor Ga *s*-like contributions). Right above this deepest band we find in Figs. 2 and 3 an experimental band close to the upper edge of the GaAs heteropolar gap. This band appears related to the theoretical band *c*. In our calculations band *c* is also close to the edge of the heteropolar gap, although only in regions close to the  $\bar{M}$  point it does not mix with the continuum. This theoretical band is due mostly to Ga  $4s$  electrons.

The two remaining experimental bands are responsible for the two leading peaks, *B* and *C*, in the local density of states. These bands have strong  $p_x p_y$  atomic orbital character. The one shallower in energy appears related to the theoretical band *e* along the  $\bar{\Gamma}\bar{X}$  direction and either to the band *f* or to the band *d'* in the  $\bar{\Gamma}\bar{X}'$  direction. Bands *e* and *f* are due to Cl  $p_x p_y$  electrons mixed to substrate  $p_x p_y$  electrons, while band *d'* is mostly due to Cl  $p_x$  electrons. The remaining experimental band appears related to bands *f* and *d''* along the  $\bar{\Gamma}\bar{X}$  line and to band *d'* along the  $\bar{\Gamma}\bar{X}'$  line. Band *d''* is a resonance again due to Cl  $p_x p_y$  electrons. Contrary to earlier suggestions,<sup>6</sup> the local density of states peak *B* corresponding to this band has prevailing  $p_x p_y$  character similar to the leading peak *C*. It is evident from Fig. 3 that the position in energy of the two experimental  $p_x p_y$  bands is in reasonably good agreement with the theoretical predictions. This explains the good agreement between theoretical and experimental positions of the leading peak in the local density of states and supports our earlier conclusions that the Cl atoms are only bound to the As atoms of the substrate.<sup>6</sup>

The comparison between theoretical and experimental band structures supports the hypothesis that the substrate atoms are displaced from their bulk positions. Relaxation displacements of these atoms induce significant changes in the theoretical band structure as illustrated by Fig. 4. This figure shows the calculated bands along the  $\bar{\Gamma}\bar{X}$  and  $\bar{\Gamma}\bar{X}'$  directions for model *B* (substrate atoms in their bulk positions) and for model *A* (substrate atoms relaxed). Several features in the experimental band structure support a relaxed configuration as in model *A*. For example, band *g* becomes much too deep compared to the corresponding experimental band when model *B* is used instead of model *A*. Another typical effect of the relaxation type of surface reconstruction is the shift to larger binding energies of band *b*. The corresponding experimental band lies in between the theoretical *b* bands given by the two models *A* and *B*. All these ob-

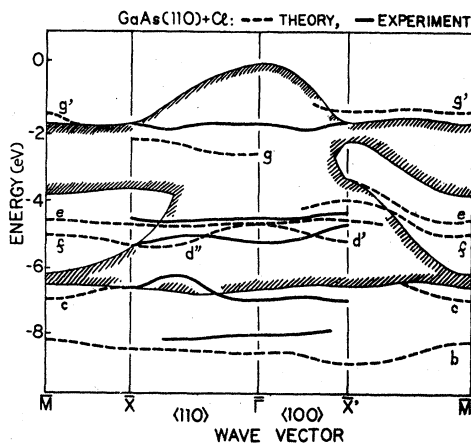


FIG. 3. Experimental band structure from Figs. 2(a) and 2(b) (solid lines) superimposed on the theoretical band structure (dashed lines) calculated using the chemisorption model *A*. The model is described in Sec. III. The shaded area corresponds to the two-dimensional projection of the bulk GaAs band structure.

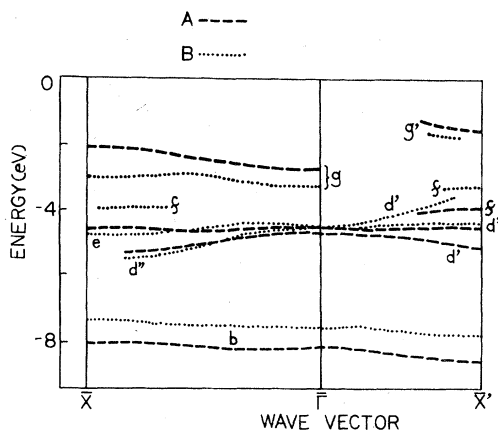


FIG. 4. Calculated band structure using the chemisorption models A and B (see Sec. III) along the  $\bar{\Gamma}\bar{X}$  and  $\bar{\Gamma}\bar{X}'$  directions.

servations lead us to the conclusion that while the substrate atoms are displaced from their bulk positions and while their displacements are qualitatively similar to those of clean GaAs (110), the magnitude of this relaxation is probably smaller than for the clean surface. Further differences can be noticed in Fig. 4 between the bands of the  $p_x p_y$  group calculated with the models A and B. The bands in the  $p_x p_y$  group, however, are too close in energy to each other to identify the best

model from these differences.

#### IV. SUMMARY

The main conclusions of our study are that the Cl adatoms on GaAs (110) are bound to the As atoms rather than to the Ga atoms and that the surface substrate atoms occupy intermediate positions between those of the bulk and those of the reconstructed clean GaAs (110) surface. The first conclusion is supported by the position in energy of the  $p_x p_y$  bands, which agrees with the charge transfer induced by Cl-As bond formation, while it would disagree with the larger charge transfer induced by a hypothetical Cl-Ga bond formation. The second conclusion regarding the qualitative feature of surface relaxation is supported by the position in energy of the Ga-As bonding  $p_z$  band and by the appearance of the Cl-induced resonance band  $\sim 2$  eV below the top of the valence band.

These results confirm that reliable qualitative information on chemisorption geometries can be obtained from angle-resolved photoemission spectroscopy techniques. Photoemission techniques provide, in general, a reliable first step toward the complete understanding of these geometries and are complementary to the more quantitative structural probes involving diffraction and wavefunction interference effects.

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