Comparison between the Electronic Structures of GaAs(111) and GaAs($\bar{1}\bar{1}\bar{1}$) from Angle-Resolved Photoemission

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Angle-resolved photoemission spectra have been measured for the polar ($\bar{1}\bar{1}\bar{1}$) and (111) surfaces of GaAs. The results show definitively that although both faces exhibit a (2×2) reconstruction, the local geometries of the unit cells must be distinctly different.

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One of the main questions in the field of semiconductor surfaces is why particular atomic arrangements or reconstructions occur on particular surfaces. In this paper we address the question by comparing the electronic properties of the (111) and ($\bar{1}\bar{1}\bar{1}$) surfaces of GaAs. This comparison is of particular interest because the ideal atomic geometry of the surfaces is the same with the species interchanged. An ideal GaAs(111) surface would be a complete Ga layer with one dangling bond per surface atom and the ($\bar{1}\bar{1}\bar{1}$) surface would have a corresponding surface of As atoms. In addition, both real surfaces exhibit a (2×2) reconstruction. Recent energy-minimization calculations[1] predict, however, that a different atomic structure occurs for each surface. The experimental results which we have obtained with angle-resolved photoemission indicate strongly that the atomic structures are significantly different for the two surfaces.

Recent work has made it clear that reconstructions can consist of much more than bond-angle distortions and that significant rearrangements of atoms occur with the creation of a surface. One of the simplest surfaces, at least in principle, is (2×1) reconstructed Si(111), but a great deal of recent work has shown that the reconstruction is much more complicated than the (2×1) symmetry might suggest. There is strong evidence[2,3] that pi-bonded chains occur on the surface layer and that there is rebonding in the second layer. The comparison which we make in this paper between the electronic properties of the two GaAs analogs of Si(111) provides significant new information about reconstruction formation on semiconductor surfaces.

A buckling model for the (2×2) reconstructed GaAs($\bar{1}\bar{1}\bar{1}$) and GaAs(111) surfaces was introduced by Haneman[4] and was used to interpret earlier photoemission results for GaAs($\bar{1}\bar{1}\bar{1}$).[5] Jakobi, Muschwitz, and Ranke[5] found surface states near 1.5 eV below the top of the valence band which they attributed to the occupied lone-pair orbital on the As atoms at the surface. Harrison[6] also discussed both surfaces and suggested that GaAs($\bar{1}\bar{1}\bar{1}$) (2×2) [GaAs(111) (2×2)] was stabilized by having $\frac{1}{4}$ monolayer of Ga (As) adsorbed on top of the double layer.

Recently, a structural model for GaAs(111) (2×2) has been put forward[7] to explain the results of LEED experiments. This model proposes that one in four of the surface Ga atoms is missing and that the remaining surface atoms undergo an inward relaxation. Total-energy calculations[1] have shown that a relaxed, vacancy surface is energetically favorable for GaAs(111) (2×2) but unfavorable for GaAs($\bar{1}\bar{1}\bar{1}$) (2×2).

(2×2) reconstructed surfaces of GaAs($\bar{1}\bar{1}\bar{1}$) and GaAs(111) were grown *in situ* by molecular beam epitaxy (MBE) from separate Ga and As effusion cells. Good (2×2) LEED patterns were also obtained for GaAs(111) surfaces produced by Ar^+ ion sputtering at 500 eV followed by annealing at 545 °C. Spectra from the MBE-produced or sputter-annealed surface showed no significant differences; however, it should be noted that the MBE-grown (111) surfaces were also annealed to 545 °C following growth to obtain the (2×2) reconstruction.

The spectra were measured at the Stanford Synchrotron Radiation Laboratory with an experimental geometry which constrained the polarization vector of the light, the surface normal of the sample, and the electron emission direction to lie in a plane. All of the data presented in this paper were collected with the photons making an angle of 45° with the sample normal. The effect of changes of the polarization direction on particular spectral features was determined and will be discussed below.

Figure 1 shows examples of angle-resolved photoemission spectra for angles approximately corresponding to the $\bar{K}_{1\times1}$, $\bar{M}_{1\times1}$, and $\bar{M}'_{1\times1}$ points of the hexagonal surface Brillouin zone. These points lie at the corner of the zone and at the two midpoints of the zone side, respectively. The $\bar{M}_{1\times1}$ and

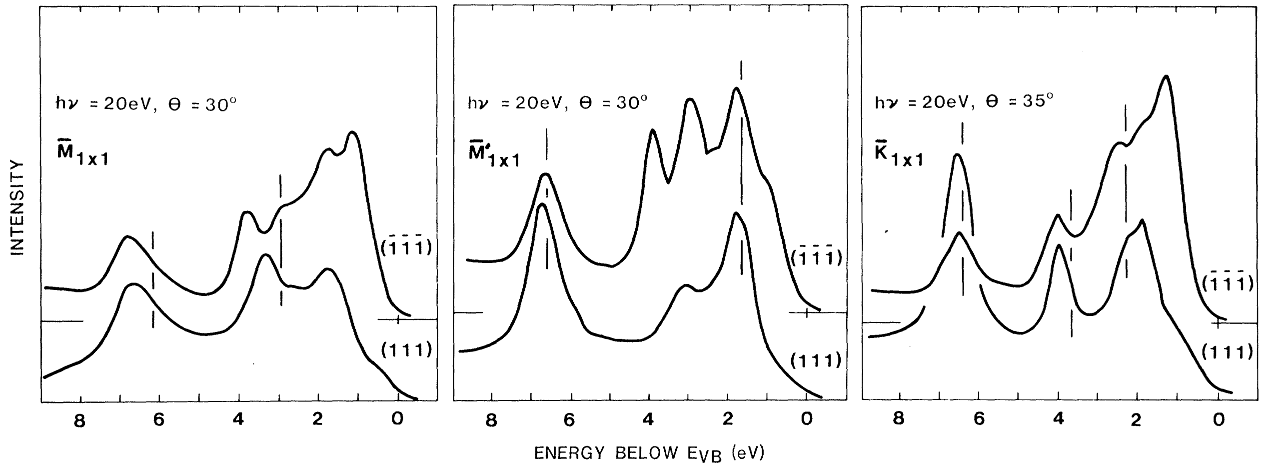

FIG. 1. Angle-resolved photoemission spectra for GaAs(111) (2×2) (lower curves) and GaAs$(\bar{1}\bar{1}\bar{1})$ (2×2) (upper curves) taken at $h\nu = 20$ eV. The spectra correspond approximately to the $\bar{M}_{1\times1}$, $\bar{M}'_{1\times1}$, and $\bar{K}_{1\times1}$ points in the surface Brillouin zone.

$\bar{M}'_{1\times1}$ points correspond to the (inequivalent) $[11\bar{2}]$ and $[\bar{1}2\bar{1}]$ directions, respectively, on the $(\bar{1}\bar{1}\bar{1})$ surface and to the $[\bar{1}2\bar{1}]$ and $[11\bar{2}]$ directions on the (111) surface. The vertical lines in Fig. 1 show the positions expected for bulk-derived features. These positions were determined from empirical pseudopotential calculations of bulk initial states and the assumption of k-conserving transitions to a (parabolic) final state whose zero of energy was placed 7.75 eV below the top of the valence band. This method has been shown previously[8,9] to give accurate agreement between experiment and theory for the (100) surface of GaAs.

Examination of the spectra in Fig. 1 shows that there are more strong features than can be explained by bulk initial states alone and that the (111) and $(\bar{1}\bar{1}\bar{1})$ surfaces have significantly different electronic properties. Differences occur not only in the region near the top of the valence band, but also in the region around 3 to 4 eV below the band edge. The strong peaks at 3.0 and 4.0 eV in the upper $\bar{M}'_{1\times1}$ spectrum in Fig. 1 are close to being degenerate with the projection of the bulk band structure onto the $(\bar{1}\bar{1}\bar{1})$ surface. Because surface-related features occur in these regions of energy and wave-vector space, location of surface states becomes rather difficult. In addition, hydrogen adsorption alters the surface stoichiometry and cannot be used to indicate surface states.[8] The method which we have chosen is to plot the positions in energy and $k_{\parallel}$ (the surface component of the wave vector) of all spectral features together with our calculations of $E(k_{\parallel})$ for the bulk states. Agreement between calculation and experiment is better than 0.5 eV and detailed results are being published elsewhere.[9] Surface-related points which remain after this procedure are plotted in Fig. 2 for two of the symmetry directions in the surface. The position in $E(k_{\parallel})$ of surface states should be independent of photon energy and the points of Fig. 2 are derived from spectra taken at a variety of photon energies.

We will first examine the results for GaAs$(\bar{1}\bar{1}\bar{1})$. Lines with a (2×2) symmetry have been drawn through some of the data points in Fig. 2. There appear to be at least two, and possibly three, surface bands within 1.75 eV of the top of the valence band. The first of these disperses down from 0.3 eV at $\bar{\Gamma}$ to 0.75 eV at $\bar{K}$ and 1.1 eV at $\bar{M}$. A second disperses upwards from 1.75 eV at $\bar{\Gamma}$ towards the zone boundary. A third band dispersing down from 0.7 eV at $\bar{\Gamma}$ to 1.35 eV at $\bar{K}$ may be present but is not drawn in Fig. 2. This band overlaps with the bulk features for small values of $k_{\parallel}$ and so can be seen best in the second of the (2×2) surface zones.

At larger binding energies, a band can be seen at 3.7 eV at $\bar{\Gamma}$ dispersing downwards towards $\bar{K}$ but having little or no dispersion in the direction towards $\bar{M}$. A peak corresponding to this band can be seen clearly in the GaAs$(\bar{1}\bar{1}\bar{1})$ spectra in Fig. 1. In all cases its relative intensity increased or remained constant with the polarization vector of the light moved towards the surface plane. This is evidence that the orbital is not aligned along the surface normal. The remaining features in Fig. 2 are not necessarily intrinsic surface bands. It was suggested earlier[8,9] that both the very flat feature near $k_{\parallel} = 0$ and 2.7 eV and the feature in the region between 5.5 and 7.0 eV may be due to transitions from bulk

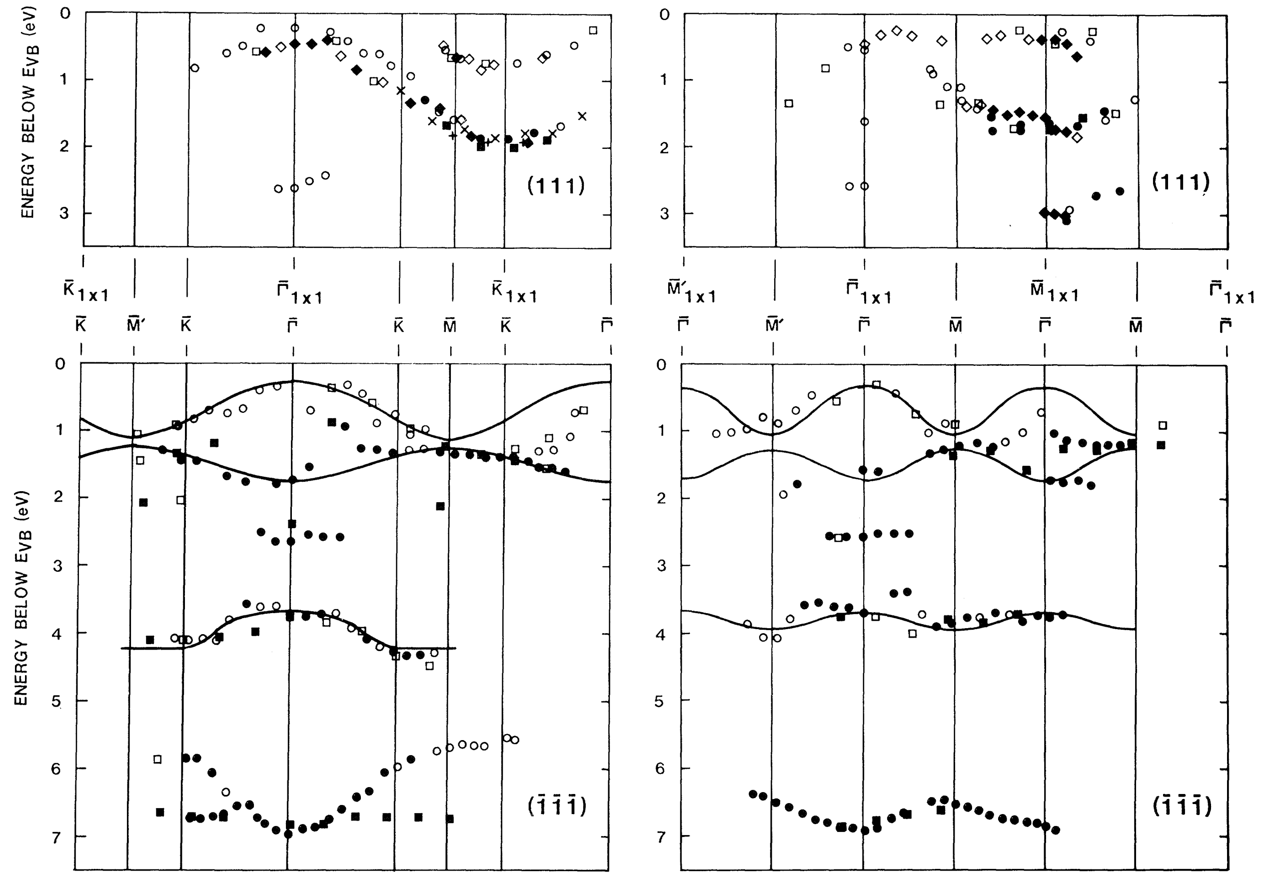

FIG. 2. Positions in energy and $k_{\parallel}$ of surface-related features from the photoemission spectra for GaAs(111) (2×2) (upper panels) and GaAs($\overline{111}$) (2×2) (lower panels). Data taken at 17, 20, 22, 25, and 27 eV are shown by lozenges, circles, crosses, squares, and pluses, respectively. Open symbols correspond to weaker features. Lines through the GaAs($\overline{111}$) data are repeated to show (2×2) symmetry.

bands which have been folded back into the (2×2) surface Brillouin zone.

We will now turn to the surface features for GaAs(111) (2×2). In contrast to GaAs($\overline{111}$) (2×2), no strong surface bands were seen at binding energies greater than 3 eV below E_{VB}. The second difference is that the features appear to have a (1×1) symmetry and not the (2×2) symmetry expected from the LEED pattern. It is possible, of course, that the surface bands do indeed have the (2×2) symmetry, but that there is only a small photoemission probability for some portion of each band. Under this assumption, bands such as those shown in Fig. 3 may be a possibility.

Surface band-structure calculations have been carried out by Nishida[10] for (1×1) GaAs(111) and GaAs($\overline{111}$) surfaces with uniformly contracted [GaAs(111)] and expanded [GaAs($\overline{111}$)] surface atomic layers. Nishida found the p_z-like dangling-bond band to be very close to the edge of the projected bulk bands for expanded GaAs($\overline{111}$) and significantly above the bulk valence band for relaxed GaAs(111). The uppermost occupied surface band in the latter case was a p_x band which was degenerate with the projected bulk bands. These findings are qualitatively consistent with the polarization de-

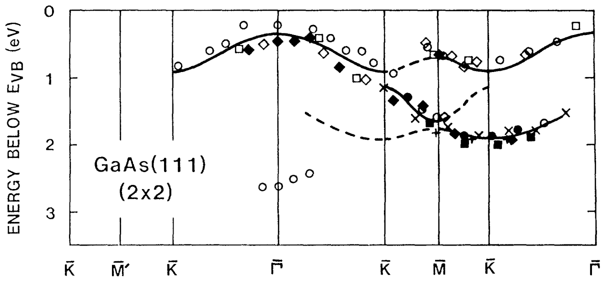

FIG. 3. GaAs(111) (2×2) data from Fig. 2 with lines showing (2×2) symmetry.

pendence of our (2×2) data. The uppermost occupied surface states near the zone boundary showed an increase (decrease) in relative intensity as the polarization vector moved towards the surface normal for GaAs$(\bar{1}\bar{1}\bar{1})$ (2×2) [GaAs(111) (2×2)].

In conclusion, the data in Fig. 2 make it clear that the electronic structures of the two surfaces are remarkably different. The origin of the difference must lie either in a different surface geometry or in the effect of interchanging Ga and As atoms. It is likely that both of these are important. There is evidence that the depth of the reconstruction or the degree of bond alteration is greater in the $(\bar{1}\bar{1}\bar{1})$ case. It was found that the agreement between the bulk calculation and the data was much closer for the (111) surface, allowing a clearer separation between bulk and surface features in the spectra.[9] The fact that the strong surface features in GaAs(111) have an apparent (1×1) repeat whereas the (2×2) symmetry is seen clearly for GaAs$(\bar{1}\bar{1}\bar{1})$ may indicate that the (2×2) potential is weaker in the (111) case. Although the true dispersion is (2×2), the non-(1×1) dispersion may be too weak to be seen, especially when degenerate with the bulk bands.

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