Atom-Selective Imaging of the GaAs(110) Surface

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We report the first voltage-dependent scanning-tunneling-microscope images of a compound semiconductor surface, GaAs(110). Images show either only Ga atoms, or only As atoms, depending on the bias voltage. By combining voltage-dependent images with theoretical calculations, we quantitatively determine surface structural parameters which cannot be inferred from the images alone.

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The scanning tunneling microscope (STM) has proven to be a powerful tool in the study of metal and semiconductor surfaces.[1] Inherently, the STM probes the *electronic* properties of a surface, with the images corresponding to contours of constant state density.[2] For metals, these contours usually just reflect the shape of the surface potential barrier, which closely follows the surface atomic positions. For semiconductors, however, a given wave function is often preferentially localized on specific atoms or bonds. Thus, the energy of a state, and its spatial distribution, may depend sensitively on both the chemical identity and the position of surface atoms.

For semiconductors, even a qualitative understanding of the STM images therefore requires consideration of the surface electronic structure. This determines, first, which states contribute to the state density at some given energy (tunneling voltage), and second, the spatial distribution of these states. Here we present the first *quantitative* analysis of the STM image of a semiconductor surface, including the dependence of the image upon both voltage and surface structure. As a result, we are for the first time able not only to identify chemically the different atoms in the unit cell, but also to determine their vertical displacements. This information cannot be obtained from a single STM image alone.

Structural analysis by STM involves, in principle, a detailed comparison of the observed images with theoretical state-density contours. In practice, this procedure is hindered by the fact that some of the observed features (such as the corrugation amplitudes) are rather dependent on both the atomic structure of the probe tip and the tip-sample separation, and these quantities are not routinely measured in the STM. It is therefore essential to identify features in the image which are sensitive to the atomic positions, but insensitive to the probe-tip structure and height.

For GaAs(110), we have identified the *difference* in lateral positions of state-density maxima between occupied and unoccupied band-edge states as a suitable feature for a structure determination. This lateral shift has a simple physical origin—occupied states are concentrated preferentially on the surface As atoms and unoccupied states on the Ga atoms.[3,4] Thus, it was theoretically predicted[4] that STM images of the occupied states should reveal the positions of the As atoms, and images of the unoccupied states should reveal the Ga atoms. This prediction is experimentally confirmed in the present work. Furthermore, we find that the precise value of the lateral shift between states is dependent on the difference in *vertical* position (buckling) of the As and Ga atoms, and by a comparison of experiment and theory we can determine an approximate value of this surface buckling. Although the STM has been used to distinguish between various models of semiconductor surfaces,[5-8] this is apparently the first quantitative determination of any structural parameter with the STM.

The tunneling microscope used in these experiments is similar to that described by Binnig and Rohrer,[1] and is described in detail elsewhere.[8] The microscope is contained in an ultrahigh-vacuum chamber with an operating pressure of $<4\times10^{-11}$ Torr. The tungsten probe tips were prepared by electrochemical etching and were cleaned *in situ* by electron-bombardment heating. The samples consisted of *n*- and *p*-type GaAs doped with Si and Zn, respectively, at a concentration of 1×10^{18} cm^{-3}. The samples were cleaved *in situ*, exposing a (110) crystal face. Spectroscopic measurements were performed by the methods of current versus voltage at fixed tip-sample separations, and voltage-dependent imaging, both of which have been previously described.[9] Computations presented here were performed with the linear augmented-plane-wave method, as described in Ref. 4.

The major results of this work concern the voltage dependence of STM images. Before that topic can be addressed, it is necessary to establish the regimes of voltage in our experiments. In Fig. 1 we show spectroscopic results obtained from clean, ordered regions of GaAs(110) surfaces. The quantity plotted, the ratio of differential to total conductivity $(dI/dV)/(I/V)$, has been shown elsewhere to provide a measure of the surface state density.[9,10] The spectra on *n*- and *p*-type material are qualitatively similar, consisting of three peaks which we label *C*, *V*, and *D*. From their location in voltage, we attribute the peak *C* with tunneling out of GaAs conduction-band states, and the peak *V* with tunneling into GaAs valence-band states. This identification is further confirmed by the observation of the spatial depen-

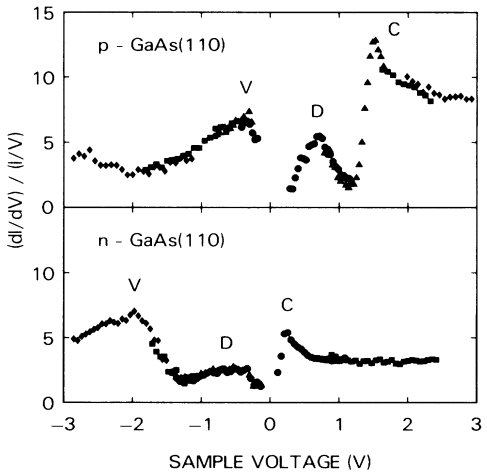

FIG. 1. Ratio of differential to total conductivity for n- and p-type GaAs. The peaks are labeled as conduction-band (C), valence-band (V), and dopant-induced (D). The different symbols refer to different tip-sample separations.

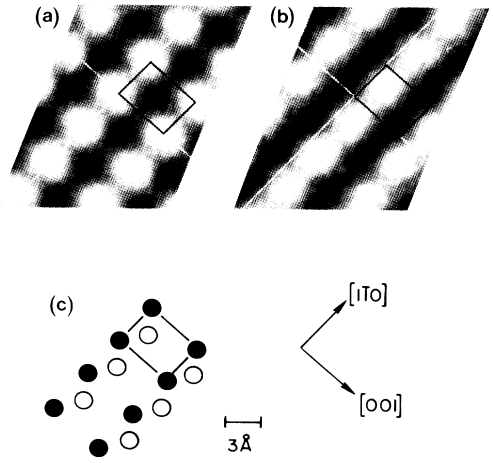

FIG. 2. Constant-current STM images acquired at sample voltages of (a) +1.9 and (b) −1.9 V. The surface height is given by a grey scale, ranging from 0 (black) to (a) 0.83 and (b) 0.65 Å (white). (c) Top view of the surface atoms. As atoms are represented by open circles and Ga atoms by closed circles. The rectangle indicates a unit cell, whose position is the same in all three figures.

dence of these peaks below. The peak D we tentatively associate with tunneling of dopant-induced carriers, i.e., tunneling out of conduction-band states on n-type material and into valence-band states on p-type material. (At the higher voltages used for imaging below, the tunneling current from the D peak makes a negligible contribution to the total current.) The separation between leading edges of the C and V peaks is roughly the band gap $E_g = 1.43$ eV, and the energy shift between n- and p-type spectra is also close to E_g, thus demonstrating that band bending in the semiconductor is small and most of the applied voltage is dropped across the vacuum gap.

In Figs. 2(a) and 2(b) we show two STM images, acquired simultaneously at voltages of +1.9 and −1.9 V. From the above discussion, these images correspond to states of the GaAs surface which are normally unoccupied and occupied respectively. A unit cell is positioned at identical locations on both images, and for comparison we show the surface-atom positions in Fig. 2(c). A shift is observed between the lateral positions of the topographic maxima in Figs. 2(a) and 2(b). This shift is easily understood by a consideration of theoretical state-density contours. For this purpose, we redraw the STM images of Fig. 2: The unoccupied states are colored green, the occupied states are colored red, and the two images are combined in Fig. 3(a). We compare these data with the theoretical state-density contours shown in Fig. 3(b). The calculation shows that the occupied state density is concentrated around the surface As atoms, and the unoccupied density around the Ga atoms.[3,4] The reason is that the As potential is more attractive than that of Ga. Thus, the observed lateral shift reflects the difference in geometric positions of the surface Ga and

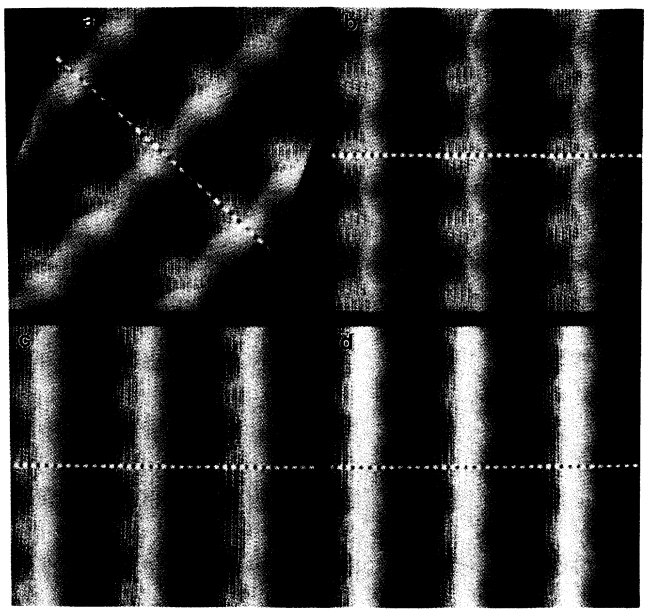

FIG. 3. Combined color images of surfaces of constant state density for occupied (red) and unoccupied (green) surface states. The intensity of each color is proportional to the height of the surface, over a range of ~1 Å. (Yellow appears where red and green overlap with roughly equal intensity.) (a) Experimental data redrawn from Fig. 2; (b)–(d) theoretical computations for buckling angles of (b) 27°, (c) 13°, and (d) 0°.

As atoms.

The spatial separation between occupied and unoccupied surface states arises from the different chemical nature of the Ga and As atoms, but it is also affected by relaxation of the surface atoms. On the GaAs(110) surface, charge transfer occurs from the Ga- to the As-derived dangling bonds, accompanied by a vertical shift in the As-atom position relative to Ga. Since the bond lengths are nearly invariant, the reconstruction may be described by a single parameter, a buckling angle ω, as pictured in Fig. 4(b). The buckling angle is believed to be about $\omega = 27°$.[11]

The charge rearrangement associated with surface buckling is illustrated in Figs. 3(b)–3(d). There, we show theoretical contours for occupied (red) and unoccupied (green) states with various amounts of buckling. The contours are for a constant state density of 10^{-8} electron/bohr^3. The unbuckled surface is metallic, and we plot the state density for all states which occur within 1 eV above or below the Fermi level. For the buckled surfaces a gap forms between occupied and unoccupied states, and the theoretical results integrate over all states within 1 eV of the band edges. The role of the electric field in the tunneling junction is small,[10] and has been neglected. Fig. 3 illustrates that, as the buckling increases, the spatial separation between occupied and unoccupied states also increases. The spatial separation observed experimentally in Fig. 3(a) is comparable to that in either Fig. 3(b) or 3(c), and is definitely greater than that for the nonbuckled surface shown in Fig. 3(d).

A more quantitative comparison between experiment and theory can be made by use of cross-sectional cuts of the state-density contours. Cuts are made along the dashed lines in Fig. 3, and the results are plotted in Fig. 4. The difference in lateral positions of state-density maxima between occupied and unoccupied states is denoted by Δ. Theoretically, we find that Δ increases by 0.84 Å as the buckling angle varies from 0° to 27°. Note that this is an electronic effect, not a geometric one; for the same variation in buckling angle the [001] Ga-As separation actually *decreases* by 0.15 Å. For the experiment shown in Fig. 4(c) we find $\Delta = 1.8$ Å. Averaging over $N = 21$ measurements performed with three different samples and probe tips, we find a mean value of $\bar{\Delta} = 2.10$ Å with a standard deviation of $\sigma = 0.37$ Å. Our estimate of the mean thus has an uncertainty of $\sigma/\sqrt{N} = 0.08$ Å The scatter in the experimental values is believed to arise from randomly varying probe-tip configurations, and also may include the effects of differing tip-sample voltages. The measurements were made at various voltages located 0.5–1.5 V from the observed surface-state extrema, and no systematic variation of Δ with voltage was observed.

In Fig. 5 we display our experimental and theoretical values of the lateral shift Δ. Theoretical values are shown for state densities of 10^{-8} and 10^{-10} electron/bohr^3, corresponding to average distances from the surface of 5.7 and 7.5 Å, respectively. The latter value is close to our best estimate of the tip-sample separation based on tunneling calculations,[9] and the former value is a conservative lower bound on the separation. The theoretical results are for an energy integration range of

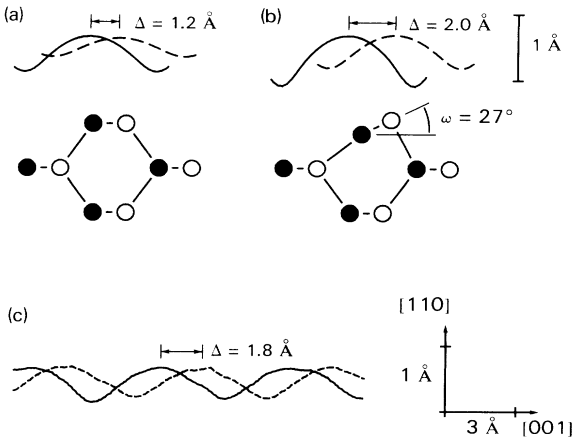

FIG. 4. [1$\bar{1}$0] cross-sectional cuts of the state-density contours for occupied (dashed line) and unoccupied (solid line) states. (Absolute height is arbitrary.) (a),(b) Theoretical results for buckling angles of (a) 0° and (b) 27°. A side view of the atomic structure is also shown, with the As atoms represented by open circles and the Ga atoms by closed circles. (c) Experimental results. The lateral shift between occupied and unoccupied states is denoted by Δ.

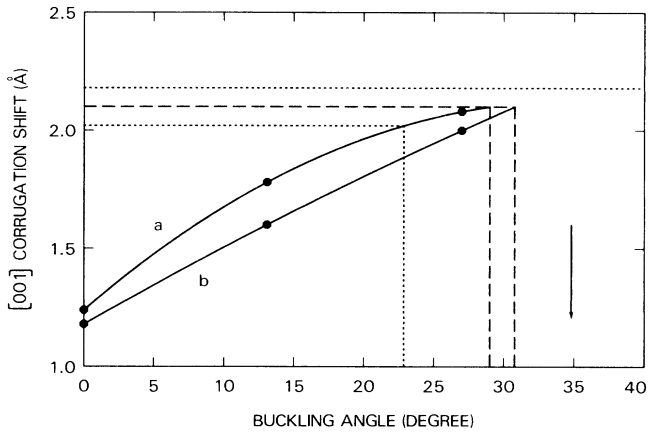

FIG. 5. Shift in lateral position between occupied and unoccupied states (Δ) vs buckling angle (ω). Experimental bounds for Δ are shown by the horizontal dotted lines, with the mean value shown by the horizontal dashed line. Theoretical curves are given by the solid lines, which are quadratics fitted to the calculated points shown, for constant state densities of (curve *a*) 10^{-8} and (curve *b*) 10^{-10} electron/bohr^3. The vertical dashed lines then give the deduced mean values for the buckling, with an uncertainty bound shown by the vertical dotted line. The arrow indicates the angle (34.8°) where the Ga bonds become planar.

1 eV; a variation of this by ± 0.5 eV changes Δ by only 0.04 Å. By combining experiment and theory, we conclude that the buckling angle is greater than 23°, with a most probable value in the range 29°–31°. As seen in Fig. 5, we cannot establish an upper bound on the buckling from our method, since Δ versus ω flattens out at large ω. However, it is physically unlikely that the buckling will be greater than 34.8° corresponding to a planar coordination of the Ga atom. This determination of surface buckling is by no means an academic exercise for GaAs(110), since its buckling was controversial until quite recently. In fact, both LEED and mega-electronvolt-ion scattering had suggested a buckling of as little as 7°.[11]

The major new result here is not the value of the surface buckling, but rather the method by which it is deduced. The buckling itself is a *vertical* distance on the surface. However, we are not able to measure this distance directly using the high vertical resolution of the STM, since the Ga and As atoms are imaged at different voltages and it is not possible meaningfully to compare vertical heights measured at different voltages. Instead, we measure the *lateral* separation Δ between state-density maxima at different voltages. By theoretically establishing a relationship between Δ and buckling, we are able to obtain a measure of the buckling. We believe that this technique will be useful for local determination of structural parameters on other surfaces as well.

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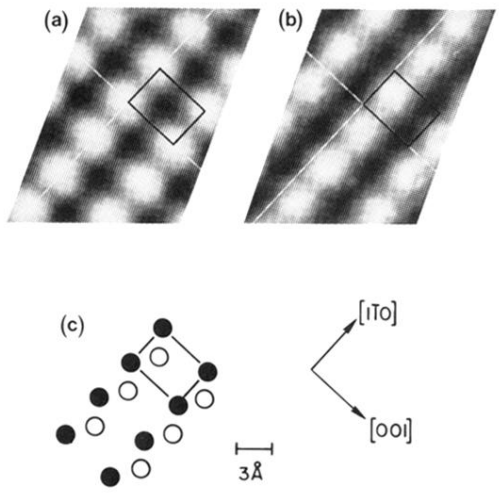

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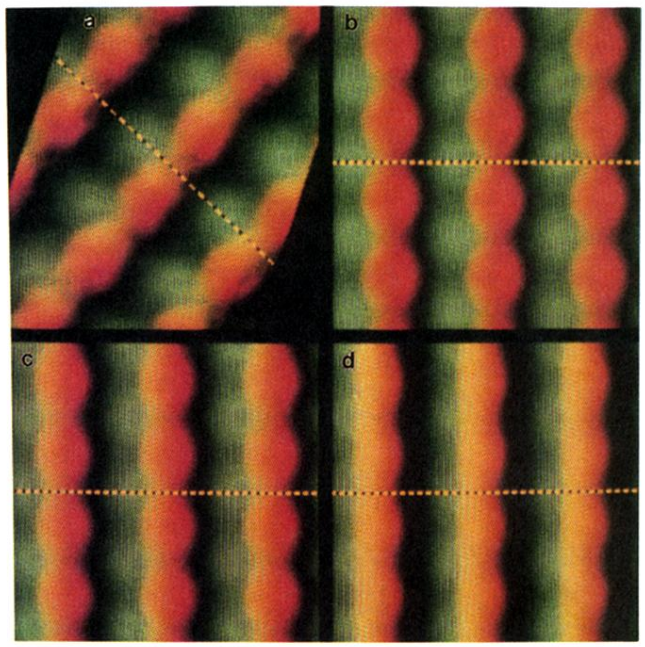

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