Local State Density and Long-Range Screening of Adsorbed Oxygen Atoms on the GaAs(110) Surface

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We report scanning tunneling microscope images of isolated oxygen atoms adsorbed on the GaAs(110) surface. The images display a dramatic voltage dependence, which arises from the energy dependence of the local state density, and provides a signature of an adsorbed electronegative atom. At low oxygen coverages, a long-range screening of the adsorbed atoms is observed in the surrounding bare surface region, with a characteristic screening length scale of ~ 50 Å.

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The scanning tunneling microscope (STM) has proven to be a powerful tool for the study of surfaces.[1] To date, most applications have concerned themselves with the study of clean or ideal surfaces. The study of multicomponent systems is a first step toward the application of STM to more sophisticated problems. The most fundamental start in this direction must deal with the question of how atoms of different chemical elements "appear" in STM images. Recent theoretical work suggests that the energy dependence of the local state density plays a crucial role in determining whether different atoms might be "visible" or "invisible," depending on the tunneling voltage used for imaging.[2]

In this Letter, we present voltage-dependent STM images of adsorbed oxygen atoms on the GaAs(110) surface, which demonstrate experimentally for the first time how the local state density is reflected in the STM images of isolated atoms. The oxidation of gallium arsenide has been a subject of considerable interest and controversy in the scientific community.[3] The application of the STM to this problem provides a unique view of the initial stages of adsorption at coverages of ~ 0.003 ML (monolayer), which is difficult to study by other techniques. The initial uptake is seen to take place on perfect terraces and does not require the presence of defects, as has been previously thought.[3] The presence of the filled $2p$ resonance of the oxygen atom is observed to give rise to both positive and negative STM contours at the adatom site, in agreement with theoretical expectations for the energy dependence of the local state density. In addition to this short-range behavior, a long-range screening is observed in the STM contours of the bare surface region surrounding the adsorbed atoms, providing a microscopic look at the local band bending at the surface.

The tunneling microscope used for this study is similar to that described by Binnig and Rohrer,[1] and is described in detail elsewhere.[4] The GaAs(110) surfaces were obtained by cleaving of n-type wavers with a 1×10^{18}-cm^{-3} Si impurity concentration, in an ultrahigh-vacuum system with a base pressure of $<4\times10^{-11}$ Torr. All images shown here were recorded with a tunneling current of 100 pA. Tungsten probe tips were prepared by electrochemical etching. Upon introduction into the vacuum system, or after oxygen exposure, the tips were cleaned by electron-beam heating and continuous scanning. This procedure eliminated any extraneous tip-related voltage drops and ensured reproducible results.

Figure 1 shows images of GaAs(110) surfaces exposed to molecular oxygen at exposures of 120 and 1480 L (1 L $=1\times10^{-6}$ Torr sec) in Figs. 1(a) and 1(b), respectively. The oxygen shows up as small protrusions on the surface, which increase in density with increased exposure, as seen in Fig. 1. Prior to oxygen exposure, large perfect terraces are observed in the STM images. The periodic array of lines or small dots in the images in Fig. 1 shows the GaAs surface; in this case the array represents the position of the As atoms, since the images were acquired at a negative sample bias corresponding to tunneling from the valence states of the sample. Conversely, tunneling at positive sample bias shows only Ga atoms, as described elsewhere.[5] This selective imaging arises from the fact that the filled states are preferentially localized on the surface As atoms whereas the unfilled states are localized on the surface Ga atoms.[6]

As seen in Fig. 1, the adsorbed oxygen appears as protrusions on the surface for tunneling out of the valence states of the sample. To investigate the energy dependence of the local state density of the oxygen, images were acquired simultaneously at different tunneling voltages, by a technique described elsewhere.[7] Figure 2(a) shows an image of one of the isolated protrusions at -2.5 V while Fig. 2(b) shows the *exact* same region of the surface at a tunneling voltage of 1.5 V. As seen in Fig. 2, the appearance of the oxygen defect is highly voltage dependent, varying from a protrusion to a surface depression.

As demonstrated in Fig. 2, near oxygen-related defects we observe an increase in the density of filled states, and a decrease in the density of empty states. This effect is very reproducible and characteristic of the adsorbed oxygen. One source of this behavior arises from the bonding character of an electronegative adsorbed atom, as seen in

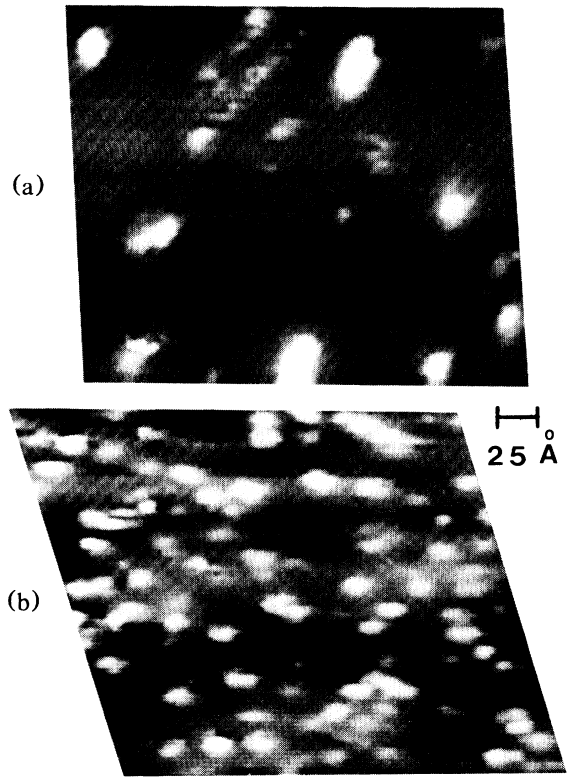

FIG. 1. Large-area STM images of the GaAs(110) surface exposed to O_2 for exposures of (a) 120 L and (b) 1480 L. The image in (b) was taken on the same surface as in (a) but with an additional exposure of 1360 L O_2. Sample voltage was −2.5 V for both images. The surface height is given by a grey scale, ranging from 0 (black) to ~3 Å (white). Oxygen coverage is estimated at 0.003 ML for (a) and 0.01 ML for (b), by counting of the number of protrusions in each image. These estimates are in agreement with previous measurements obtained with conventional methods (Ref. 3).

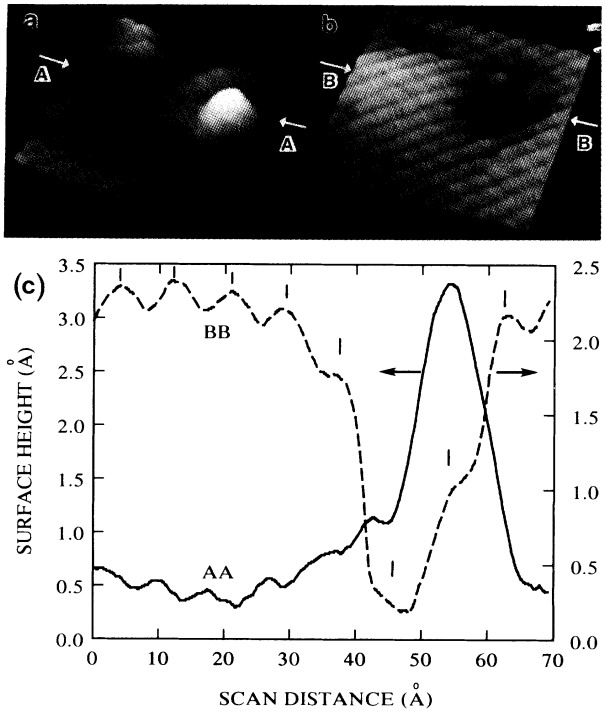

FIG. 2. STM images of an oxygen defect acquired simultaneously at sample voltages of (a) −2.6 V and (b) 1.5 V. (c) Surface-height contours along the lines AA (solid line) and BB (dashed line) shown in (a) and (b), respectively. (Absolute height is arbitrary.) Oxygen exposure is 120 L. The tick marks indicate the position of the Ga lattice.

recent theoretical calculations.[2] Lang has shown how an electronegative adsorbate has an enhanced state density below the Fermi level and correspondingly a depleted state density above the Fermi level, leading to highly voltage-dependent STM contours.[2] We expect this behavior to be spatially localized within a radius of 5–10 Å around the defect.[2,8] We note that the maxima of the contour AA in Fig. 2 do not coincide with the minima of contour BB, thus demonstrating that the enhanced and depleted states are not spatially coincident.

In addition to the "chemical effects" discussed above, an electrostatic effect is observed encompassing the oxygen defects. The oxygen adsorbates will tend to acquire electrons to fill their $2p$ level, and thus will have a net negative charge. This negative charge will repel the conduction-band electrons, and a depletion region is formed around each adsorbate. Outside this depletion region, the field from the charged defect is screened by the conduction electrons with a characteristic length given by

$$L=\{[\epsilon k_B T \mathcal{F}_{1/2}(\eta)]/[4\pi n e^2 \mathcal{F}_{-1/2}(\eta)]\}^{1/2},$$

where ϵ is the static dielectric constant, n is bulk electron concentration, $\mathcal{F}_k$ is the Fermi integral of order k, and $\eta=E_F/k_BT$ is the reduced Fermi energy.[9] For GaAs with an impurity concentration of 1×10^{18} cm^{-3} we obtain $L=56$ Å.

The Coulomb field from the charged adsorbate modifies the surface state density of the semiconductor; in a semiclassical picture this may be viewed as band bending, and quantum mechanically the effect is described by scattering from a Coulomb potential. For conduction-band states (electrons) the potential is repulsive, leading to a decrease in the band-edge state density, and for valence-band states (holes) the potential is attractive leading to an increased state density.[10] This change in state density in turn affects the tunneling current and constant-current contours. The contours in Fig. 2(c) display this electrostatic effect. The change in contour height is large for a radius of 10–20 Å around the defect, and has a tail extending to a radius of ~50 Å, in agreement with the above estimate for the screening length. The atomic configuration (shown by the tick marks on contour BB) can be seen superimposed on top

of this slowly varying envelope. The fact that the curvature of the bare surface is either positive or negative, depending on tunneling bias, shows that this effect is purely electronic and does not correspond to a geometric distortion of the surface. The range of the electrostatic perturbation is more clearly seen in the defects shown in Fig. 3. Figure 3(b) shows the two contours along the lines AA and BB in Fig. 3(a). The field of the charged defect produces in this case both an *increase* in the contour height near the defect as well as a *reduction* in contour height at large distances from the defect. This oscillatory nature of the contour, observed only at negative bias, occurs as a result of competing components in the tunneling current, as demonstrated by the spectroscopic results presented below.

The STM contours observed around the defects are, in effect, a real-space view of the local band bending produced in response to the field introduced by the defects. The (110) surface of GaAs maintains flat bands upon cleavage and the adsorption of oxygen is observed to cause band bending.[3] This band bending at the surface can be directly observed in the current-voltage (I/V) measurements on the oxygen-covered surface, as shown in Fig. 4. Before oxygen exposure the I/V measurements on the clean surface are characteristic of a degenerate semiconductor and show an onset for tunneling at both the small-positive- and -negative-voltage regions, which can be understood from the band diagram for the clean surface in Fig. 4.[11] Current at 0+ voltages occurs through tunneling into the empty conduction-band states, while current at 0− voltages occurs as a result of tunneling out of conduction-band states which are occupied because of the n-type doping. The latter component of the current is labeled D in Fig. 4. The band bending on the oxygen-exposed surface can be seen in the I/V curve as a gap opening up at low voltages. The onset current for tunneling into the conduction band shifts from 0 to approximately 0.5 V. The upward shift of the bands also pinches off the D component of the current, as illustrated in the band diagram for the oxygen-covered surface in Fig. 4. A shift in the valence-band onset is slightly obscured since the clean-surface I/V contains the current from the D channel, but the onsets can be approximately located as −1.5 V on the clean surface and −1 V on the oxygen-covered surface.

The local band bending on the surface can be investigated spatially, with I/V measurements taken in the vicinity of the oxygen defects, as shown in Fig. 5. In Fig. 5(a) an oxygen defect is observed at the left of the figure with the familiar depressed region surrounding it. I/V measurements taken at positions 1–4 are shown in Fig. 5(b), where we focus on the D component of the current in the range 0 to −2 V. The transition from the flat bands observed on the clean surface, in Fig. 4, to the

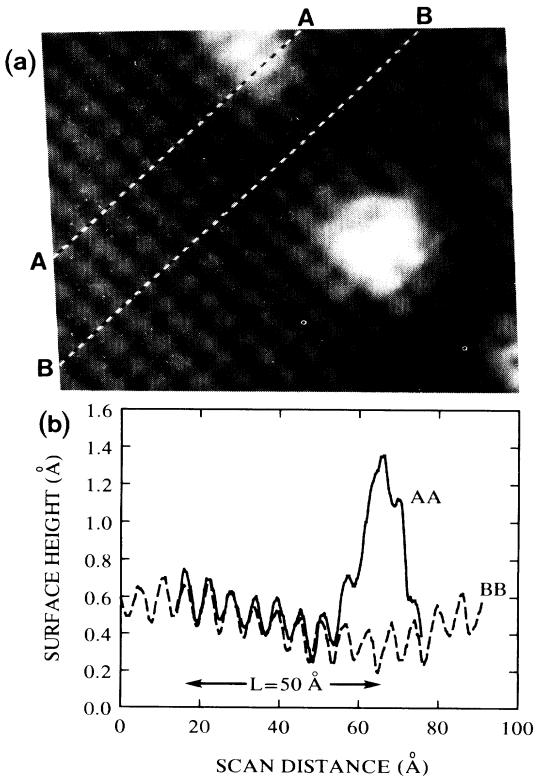

FIG. 3. (a) STM image of defects on GaAs(110) at −2.5 V sample bias. (b) Surface-height contours, in the [001] direction, along the lines AA (solid line) and BB (dashed line) shown in (a).

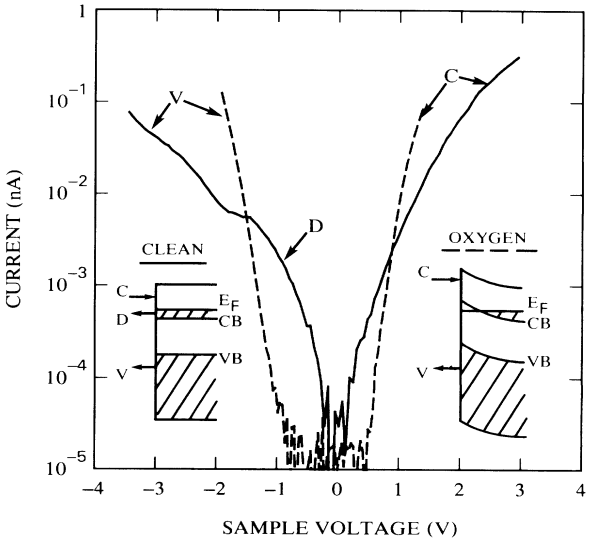

FIG. 4. Current-voltage measurements obtained in the clean GaAs(110) surface (solid line), and on the oxygen-exposed surface in Fig. 1(b) (dashed line). Insets: The band diagrams for the clean and oxygen-covered surfaces; current components are labeled C, conduction band; V, valence band; and D, dopant induced.

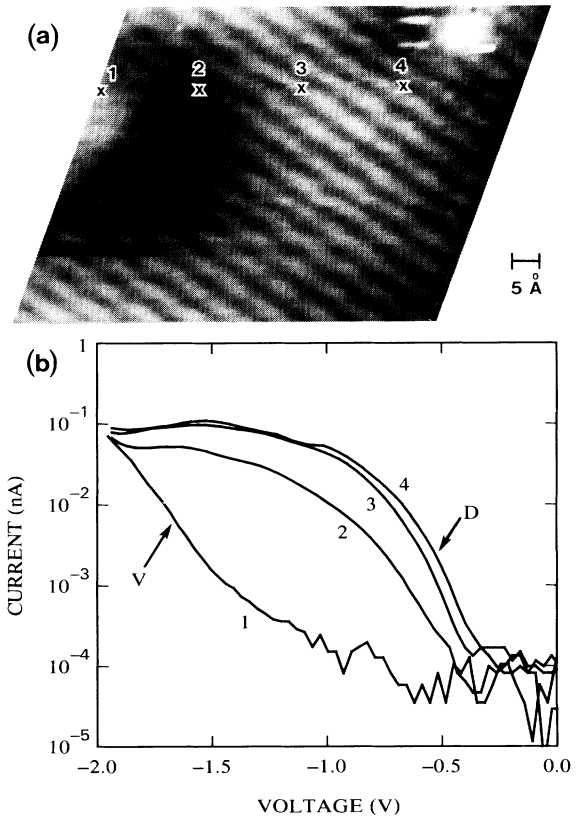

FIG. 5. (a) STM image of an oxygen defect at −2 V sample bias. Oxygen exposure is 30 L. (b) Current-voltage measurements obtained simultaneously with the image (a) at the four points indicated in the image.

pinned oxygen-covered surface can be observed in the sequence of I/V's. Far from the defect the current turns on at low negative voltages because of the D channel, similar to that seen on the clean surface in Fig. 4. As we approach the defect, the bands bend upward with a decrease in the D component of the current, as observed in I/V's No. 1 and No. 2. Note that this component decreases in I/V No. 2 even though the tip moves closer to the surface. This elucidates the mechanism by which the band bending is observed in the STM contours at negative voltage. It is the decrease in the D component of the current which causes the tip to move closer to the surface, giving rise to the depressed regions far from the defects. As the D component decreases, the V component of the current will increase because of an enhanced valence-band surface state density. This effect is dominant close to the defect, and the STM contour then increases.

In conclusion, we have shown how the STM contours of isolated oxygen atoms, adsorbed on the GaAs(110) surface, reflect the energy dependence of the local state density. This dependence is characterized by an increase in state density below the Fermi level at the expense of a decrease of unoccupied state density, characteristic of an electronegative adsorbate. A microscopic observation of the local band bending produced by the oxygen is seen in the STM contours, with a long-range screening length of ~50 Å.

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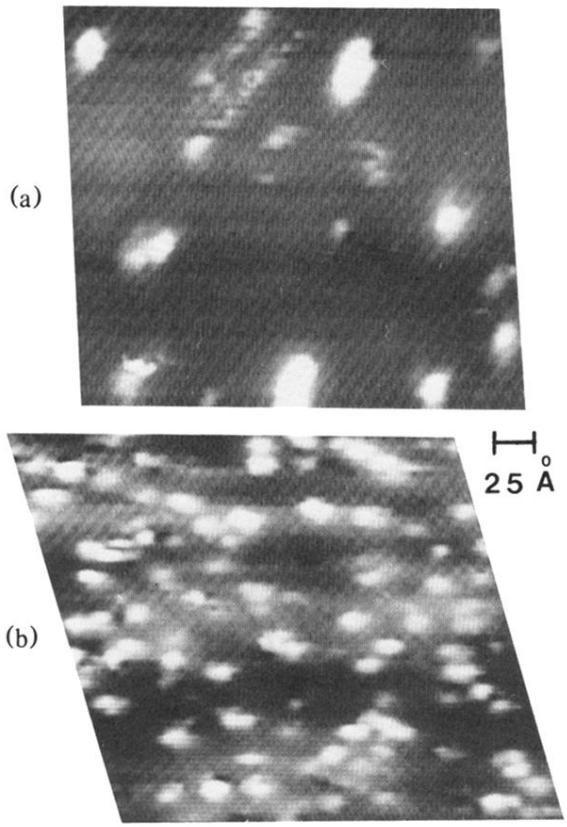

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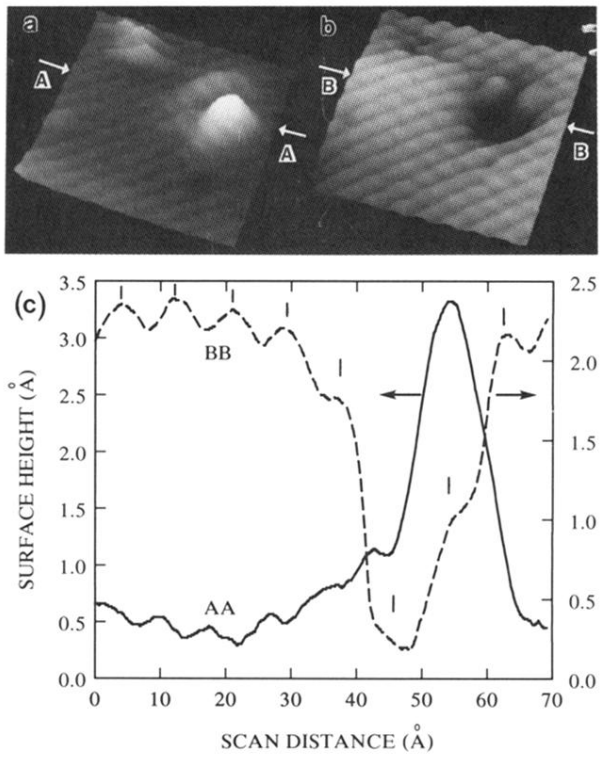

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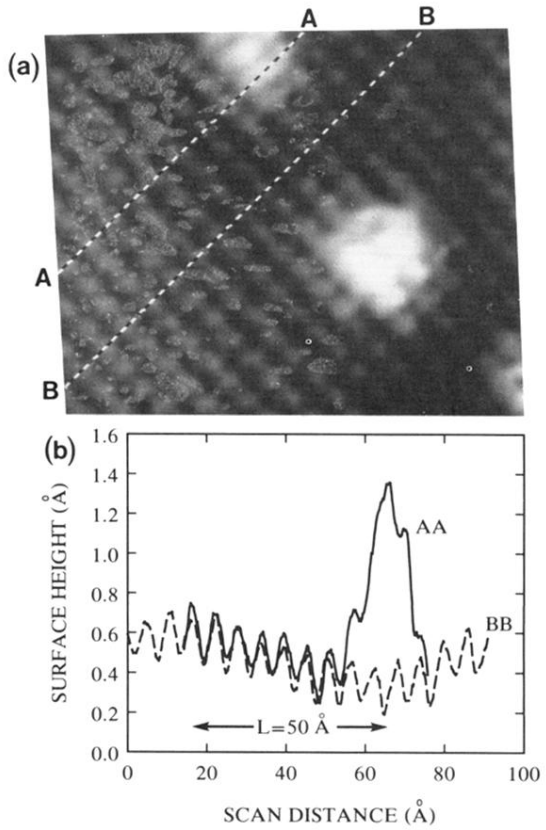

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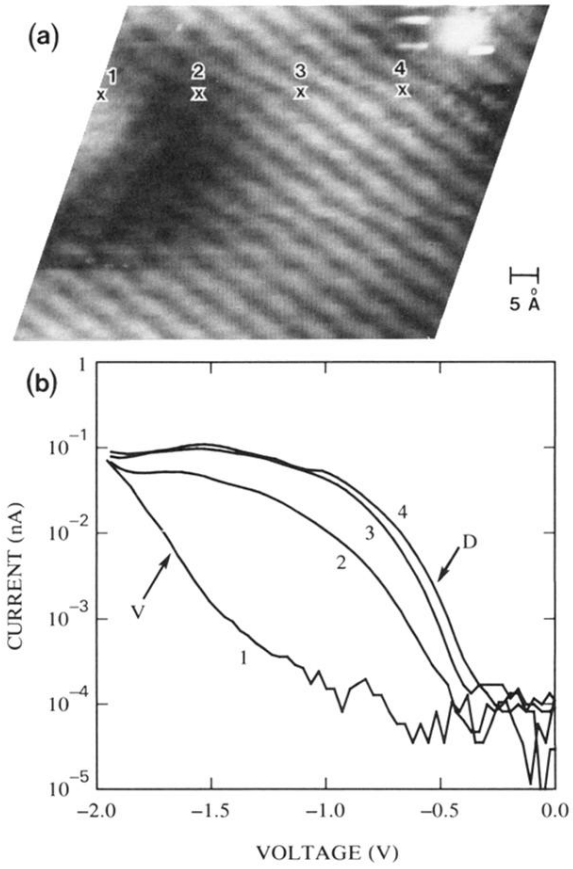

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