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Structure of oxygen adsorbed on the GaAs(110) surface studied using scanning tunneling microscopy

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We report results, from scanning tunneling microscopy, on the initial phase of oxygen adsorption on *p*-type GaAs(110) surfaces. High-resolution measurements show that atomic oxygen is bonded in an interchain bridging position. The results on *p*-type material show no evidence for band bending and are in marked contrast to previous results observed on *n*-type GaAs(110) surfaces.

The nature of the interaction of oxygen with the GaAs(110) surface has been a subject of considerable interest and controversy.[1-14] Many studies have tried to address the specific questions as to whether the initial adsorption is molecular or atomic, the binding site As or Ga, and as to what is the mechanism for the observed Fermi-level pinning. A review of the literature leads to many conflicting viewpoints based on many different experimental and theoretical results. Some of the main experimental facts are (1) the adsorption of oxygen proceeds in at least two distinct phases, with the initial phase being slower and saturating at a coverage of ≤ 0.1 monolayer (ML),[9,11] (2) during this initial-phase electron-energy loss spectroscopy (EELS) data show a progressive decrease in the Ga 3*d* loss peak,[3,11] and (3) photoemission measurements show the As 3*d* core levels developing a sequence of shifts during the second more rapid uptake phase.[2,9] Theoretical calculations favored adsorption on single As sites at low coverages and agreed with the core level shifts observed in the As 3*d* photoemission spectra.[6-8] The sensitivity of the Ga 3*d* loss peak in the initial adsorption of oxygen was countered theoretically[6-8] by suggesting the Ga sensitivity was due to Ga bonded to As, which in turn is bonded to oxygen, or was explained as due to adsorption at surface defect sites,[9,11] as this phase was observed to be cleavage dependent. Various other adsorption models, involving more complicated geometries, have also been proposed to explain the data, most of which come from the higher coverage phases. The exact nature of the initial phase of oxygen adsorption on the GaAs(110) surface remains unresolved.

In this Communication, we present new results from scanning tunneling microscopy (STM) on oxygen adsorption on *p*-type GaAs(110), which are in marked contrast to earlier results on *n*-type GaAs(110).[14] From this comparison a detailed microscopic picture of the nature of oxygen adsorption of the GaAs(110) surface is obtained. Specifically, these new results on *p*-type GaAs(110) show that in the initial phase of oxygen adsorption (1) isolated oxygen atoms are adsorbed on the GaAs(110) surface on defect-free terraces, (2) the oxygen is bonded in an interchain bridging site, aligned in the $[1\bar{1}0]$ direction with the surface As atoms, and (3) the adsorbates appear to be negatively charged on *n*-type material, and neutral on *p*-type material.

The tunneling microscope used for this study is similar to that developed by Binnig and Rohrer,[15] and is described in detail elsewhere.[16] The microscope is contained in an ultrahigh vacuum system with a base pressure of $<4\times10^{-11}$ Torr. The GaAs(110) surfaces were prepared by cleaving in vacuum *p*-type wafers with a 1×10^{18} cm^{-3} Zn impurity concentration. All images shown here were recorded with a tunneling current of 100 pA. The images are shown uncorrected for piezo drift, with $[1\bar{1}0]$ crystallographic axis at 45° with respect to the horizontal direction. 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 or continuous scanning. This procedure eliminated any extraneous tip related voltage drops and ensured reproducible results.

Figure 1 shows STM images recorded on *p*-type GaAs(110) for different exposures of oxygen. Figure 1(a) shows a large 140×140-Å^2 image of the clean surface free of defects (the abrupt changes in contrast in the image are due to probe tip changes). Generally the STM images reveal large defect-free terraces on the GaAs(110) surface. The array of dots in Fig. 1(a) define the position of the As atoms in the 4.0×5.65-Å^2 unit cell. The relative prominence of the As atoms reflects the greater electronegativity of the As.[17] That is, probing filled states reveals the As atoms, whereas probing the empty states reveals the Ga atoms. At low oxygen exposures, small isolated protrusions appear in the images, as shown in Figs. 1(c) and 1(d). At higher exposures the density of protrusions increases, as shown in Fig. 1(b).

Figure 2 shows a sequence of images of a single oxygen adsorbate acquired simultaneously by sequencing the sample voltage in the line scans, as described previously.[18] The bottom three panels are taken at negative sample bias corresponding to tunneling out of the filled electronic states, while the top three panels are at positive sample bias corresponding to tunneling into empty states. We expect the apparent size (height) of the adsorbate to be energy dependent, due to the energy dependence of the density of states.[19] This is more clearly seen in the lower part of the figure where the contours going through the oxygen adsorbate are plotted.

The measurements in Fig. 1, which were on *p*-type material, differ significantly from results previously observed

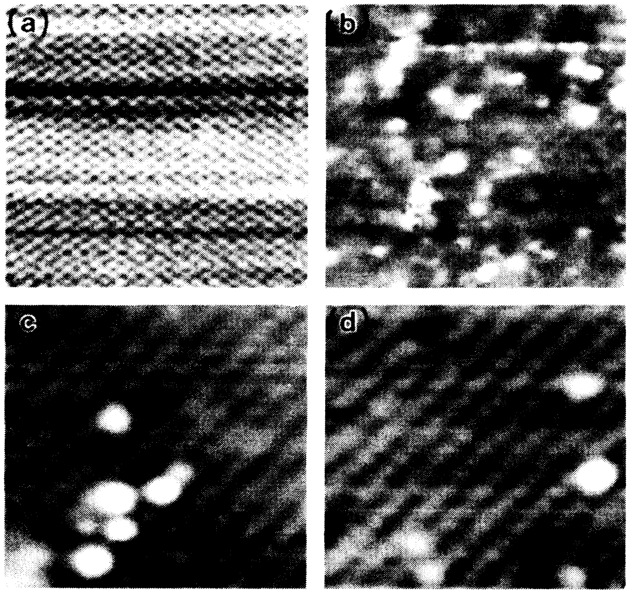

FIG. 1. STM images of the p-type GaAs(110) surface exposed to O_2. (a) 140×140 $Å^2$ image of the clean surface. (b) 140×140 $Å^2$ image of a surface exposed to 5000 L (1 langmuir $= 10^{-6}$ Torrs) of O_2. (c), (d) 70×70 $Å^2$ image of a surface exposed to 800 L O_2. Sample voltage was -2.4 V for (a), -3.3 V for (b), -3.0 V for (c), and -2.8 V for (d). Surface height is given by a grey scale, ranging from 0 (black) to ~ 2 Å (white).

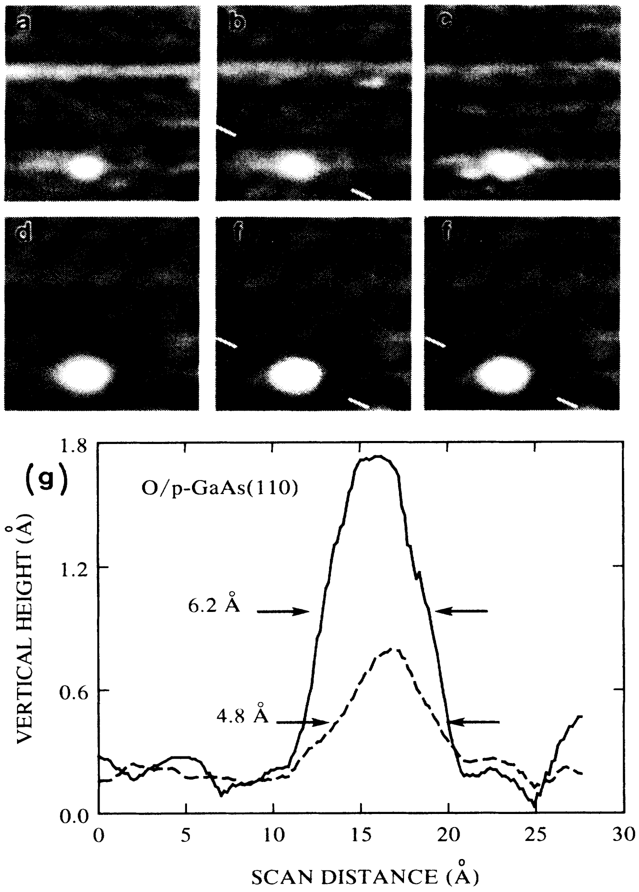

FIG. 2. STM images of an oxygen atom on p-type GaAs(110) acquired simultaneously at sample voltages of (a) 1.9 V, (b) 2.5 V, (c) 3.0 V, (d) -3.5 V, (e) -3.0 V, and (f) -2.8 V. (g) STM contours in the [001] direction, indicated by the tic marks at the edge of the figures, for the oxygen adsorbate in (f) (solid line) and (b) (dashed line). O_2 exposure was 800 L.

on n-type material.[14] In the p-type measurements in Fig. 1 the isolated adsorbates are very small in lateral size, and always form protrusions on the surface. In comparison, on n-type GaAs the oxygen-related features are significantly delocalized encompassing many surface unit cells, and both positive and negative tip displacements are observed. We have interpreted the n-type results in terms of a negatively charged center producing band bending at the semiconductor surface.[14,20] The band bending on n-type GaAs has also been observed with the STM in current-voltage measurements. The small size and the lack of the negative contours at positive sample bias on p-type GaAs indicates a neutral center with little or no surface band bending. The absence of band bending on p-type GaAs is consistent with current-voltage measurements, presented elsewhere,[20] and is in agreement with photoemission results.[12] We interpret these results in a model where the negative charge on the adsorbate resides in valence band states. In p-type material this negative charge is screened by an accumulation of holes, and the adsorbate thus appears to be neutral. Although the precise nature of the oxygen-related electronic states is not known at present, it is not required for the structural analysis presented below.

The STM contours of the oxygen on p-type GaAs in Figs. 1 and 2 display a lateral size of 4–6 Å full width half maximum (FWHM). The expected lateral size of a single oxygen atom from theoretical calculations of STM contours of chemisorbed atoms is in the range of 5-6 Å FWHM.[21] This good agreement with the observed experimental contours, together with the spherical shape of the observed contours, would suggest that the STM images of these surface protrusions correspond to single adsorbed atoms, as opposed to O_2 molecules or more complicated structures involving reconstructed Ga and As atoms. Molecular adsorption of O_2 also seems unlikely based on recent low-temperature photoemission measurements, which have shown that molecular O_2 weakly physisorbs only below 50 K on the GaAs(110) surface.[10] In addition, for an O_2 molecule one would expect a node, which is not observed, in the center of molecule in the STM contour of the unoccupied states. We therefore interpret the protrusions in the STM images as corresponding to single oxygen atoms.

The lack of the band-bending effects on p-type GaAs allows high-resolution measurements to be made, in which the registry of the surrounding surface can be used to pin-point the location of the isolated charge density maximum. Figure 3(a) shows an image of one of the isolated oxygen atoms where the surface corrugation is visible along both directions of the surface unit cell. In Fig. 3(b)

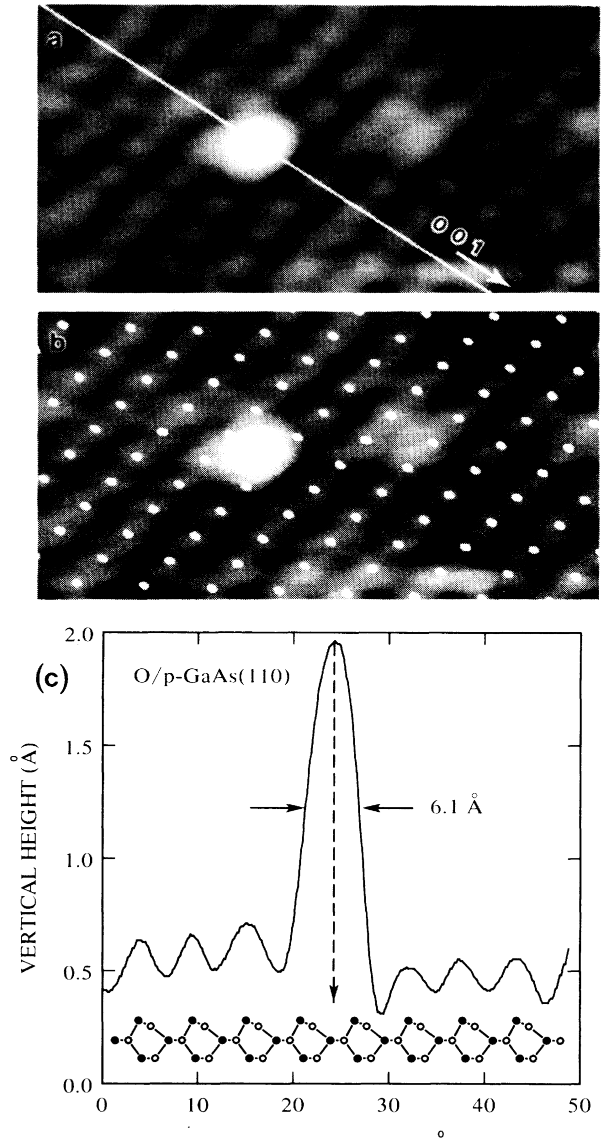

FIG. 3. (a) 70×40 $Å^2$ STM image of an isolated oxygen atom on a *p*-type GaAs(110) surface taken at -2.8-V sample bias. The solid line is drawn through the As maxima in the [001] direction. (b) Same as (a), with the (110) surface unit mesh superimposed, showing the position of the surface As atoms. (c) Surface height contour through the oxygen atom along the cut shown in (a). A side view of the GaAs(110) surface is shown in the lower part of (c).

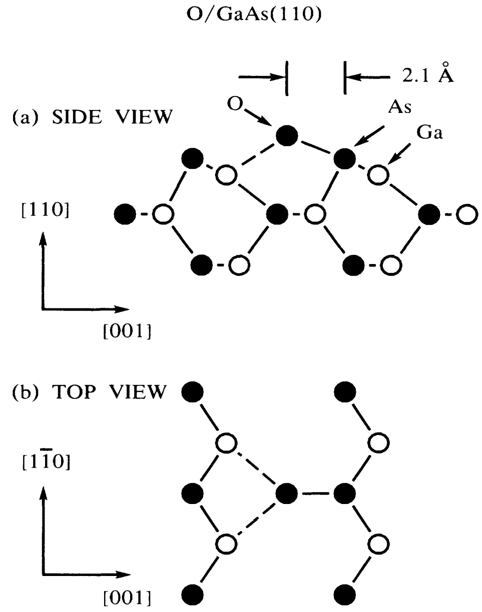

FIG. 4. (a) Side view of the GaAs(110) surface with the deduced position of the adsorbed oxygen from Fig. 3. (b) Top view.

the image is displayed with a superimposed grid indicating the position of the As atoms. Previous theoretical calculations have shown that the position of the maxima in the corrugation are within 0.15 Å of the As lattice positions.[17] From Fig. 3(b) the oxygen adsorbate can be located relative to the As atoms; in the [1$\bar{1}$0] direction the adsorbate is coincident with an As row, and in the [001] direction the adsorbate is located in between two As rows. Most of the adsorbed oxygen atoms can be observed on a similar site in this low coverage phase, as seen in Figs. 1 and 2. A more precise location in the [001] direction is determined from examining the position of the oxygen maximum in the contour along the [001] direction, as shown in Fig. 3(c). A model of the GaAs(110) surface geometry is shown in the lower part of the figure for comparison. From the As positions in the contour in Fig. 3(c) we determine the position of the oxygen maximum to be located at 2.1 ± 0.3 Å relative to the first neighboring As atom in the [001] direction. This indicates the oxygen is bonded in an interchain bridging position roughly equidistant from a single As atom and two Ga atoms in the neighboring chain, as shown in Fig. 4.

The located position of the oxygen in Fig. 4 indicates a configuration where the oxygen is bonded to both As and Ga atoms. Previous cluster calculations have shown that the high electronegative oxygen would prefer bonding to single As atoms over Ga atoms.[7,8] A stable configuration was obtained where the As lone pair acts as an electron donor into an unoccupied 2*p* orbital of the oxygen. A relatively short bond length of 1.63 Å was found for this configuration. This bond length would correspond to a lateral distance of the oxygen from the As site of 1.35 Å, which is significantly smaller than the 2.1 Å observed in the present results. The observed bond lengths are also slightly larger than expected based on bulk oxides where the As—O bond length is 1.8 Å.[22] A longer bond length could result from an interaction of the two other occupied *p* orbitals of the oxygen with the two neighboring Ga atoms, each of which have an empty orbital that would accept electron donation. This bonding configuration might also explain the sensitivity of the Ga 3*d* loss peak in the EELS data[3,11] in the initial adsorption phase.

An exact determination of the bond lengths cannot be made from the STM data alone, as slight rearrangements of the oxygen bonded surface atoms may take place, e.g., towards an unbuckled geometry,[7] or the maximum in the oxygen charge density may not be exactly coincident with the atomic location.[17] As far as we know the bonding geometry shown in Fig. 4 has not been tested theoretically, and further calculations for both atomic and molecular oxygen in this geometry would prove useful in understanding this initial chemisorption phase of oxygen on the GaAs(110) surface.

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[1] R. Dorn, H. Luth, and G. J. Russell, Phys. Rev. B **10**, 5049 (1974).

[2] P. Pianetta, I. Lindau, C. Garner, and W. E. Spicer, Phys. Rev. Lett. **35**, 1356 (1975); **37**, 1166 (1976).

[3] R. Ludeke, Solid State Commun. **21**, 815 (1977).

[4] J. Stöhr, R. S. Bauer, J. C. McMenamin, L. I. Johansson, and S. Brennan, J. Vac. Sci. Technol. **16**, 1195 (1979).

[5] C. R.Brundle and D. Seybold, J. Vac. Sci. Technol. **16**, 1186 (1979).

[6] E. J. Mele and J. D. Joannopoulos, Phys. Rev. B **18**, 6999 (1978).

[7] J. J. Barton, W. A. Goddard, and T. C. McGill, J. Vac. Sci. Technol. **16**, 1178 (1979).

[8] J. J. Barton, A. Swarts, W. A. Goddard, and T. C. McGill, J. Vac. Sci. Technol. **17**, 164 (1980).

[9] C. Y. Su, I. Lindua, P. W. Chye, P. R. Skeath, and W. E. Spicer, Phys. Rev. B **25**, 4045 (1982).

[10] D. J. Frankel, J. R. Anderson, and G. J. Lapeyre, J. Vac. Sci. Technol. B **1**, 763 (1983).

[11] F. Bartels and W. Monch, Surf. Sci. **143**, 315 (1984).

[12] G. Landgren, R. Ludeke, Y. Jugnet, J. F. Morar, and F. J. Himpsel, J. Vac. Sci. Technol. B **2**, 351 (1984).

[13] R. Haight and J. Bokor, Phys. Rev. Lett. **56**, 2846 (1986).

[14] J. A. Stroscio, R. M. Feenstra, and A. P. Fein, Phys. Rev. Lett. **58**, 1668 (1987); J. A. Stroscio, R. M. Feenstra, D. M. Newns, and A. P. Fein, in *Proceedings of the Second Conference on Scanning Tunneling Microscopy/Spectroscopy, Oxnard, CA, 1987* [J. Vac. Sci. Technol. A (to be published)].

[15] G. Binnig and H. Rohrer, Helv. Phys. Acta **55**, 726 (1982); Surf. Sci. **152/153**, 17 (1985).

[16] R. M. Feenstra, W. A. Thompson, and A. P. Fein, Phys. Rev. Lett. **56**, 608 (1986); J. Vac. Sci. Technol. A **4**, 1315 (1986).

[17] R. M. Feenstra, J. A. Stroscio, J. Tersoff, and A. P. Fein, Phys. Rev. Lett. **58**, 1192 (1987).

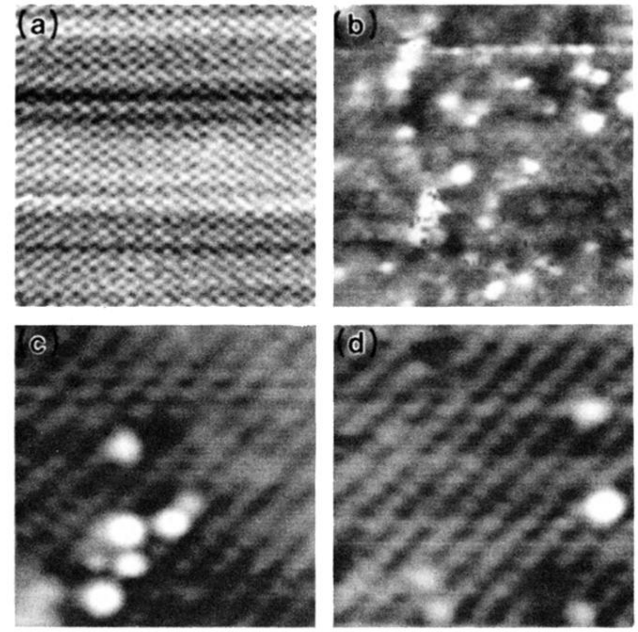
[18] J. A. Stroscio, R. M. Feenstra, and A. P. Fein, Phys. Rev. Lett. **57**, 2579 (1986); J. Vac. Sci. Technol. A **5**, 838 (1987).

[19] N. D. Lang, Phys. Rev. Lett. **58**, 45 (1987).

[20] J. A. Stroscio and R. M. Feenstra (unpublished).

[21] N. D. Lang, Phys. Rev. Lett. **56**, 1164 (1986).

[22] R. W. G. Wykoff, *Crystal Structures* (Interscience, New York, 1974).



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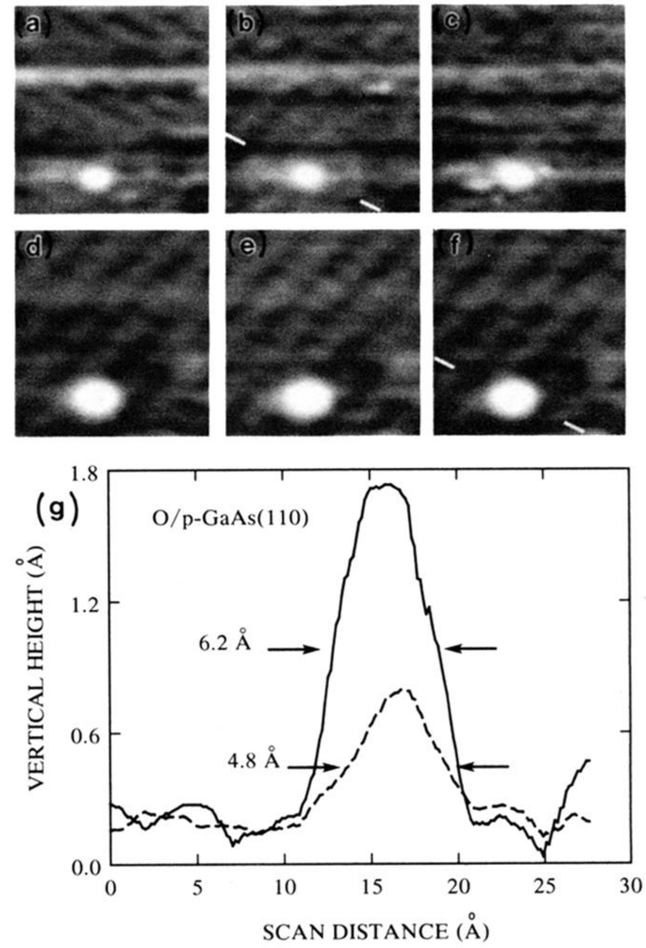

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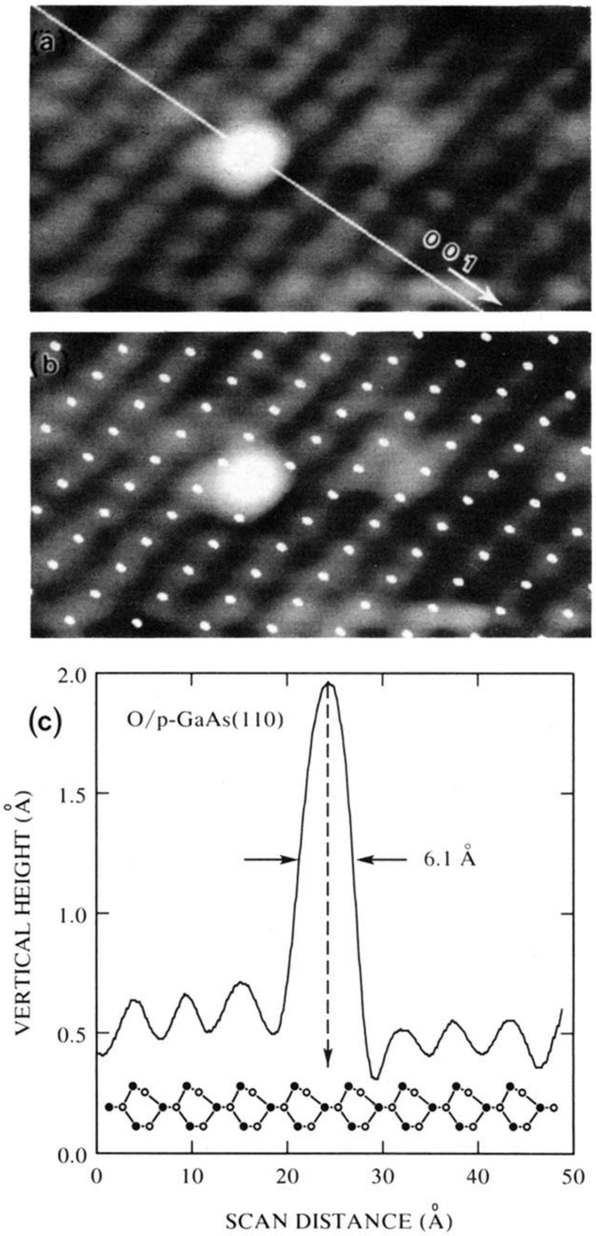

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