PHYSICAL REVIEW B VOLUME 17, NUMBER 8 15 APRIL 1978

Surface bond angle and bond lengths of rearranged As and Ga atoms on GaAs(110)

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(Received 12 July 1977)

We have determined the surface structure of GaAs(110) by comparing our experimental low-energy-electron-diffraction (LEED) data with curves calculated by the combined space method. We find that the best agreement between theory and experiment is obtained for a structure in which the As atoms are tilted outward and the Ga atoms are tilted inward, with an angle of rotation of 27° and a Ga to second-layer spacing of 1.452 Å. For this structure the As back bond is contracted by about 5%. These findings are compared with previous results from LEED and surface-band-structure calculations.

I. INTRODUCTION

There has been a great deal of attention focussed on the electronic structure of the GaAs(110) surface. It is now generally agreed that photoemission measurements indicate the existence of a rather broad anion-derived surface band near the valence-band maximum and an empty cation-derived band located above the conduction-band minimum. In other words, there are no intrinsic surface states within the band gap.[1-4] These experimental results are in contradiction to findings of early theoretical band calculations,[5] which show a sharp and much narrower anion surface-state peak at the valence-band maximum and cation surface states with energies falling within the band gap. Rowe *et al.*[6] proposed that some of these photoemission results might be explained by assuming that the surface atoms are rearranged. This suggestion is in agreement with much earlier qualitative low-energy-electron-diffraction (LEED) observations by MacRae and Gobeli.[7,8] The structure proposed by Rowe *et al.* was that the Ga atoms relax inward and the As atoms relax outward.[9,10] Similar surface-atom rearrangements were arrived at by Harrison[1] and by Spicer *et al.*,[1] who concluded that in this relaxed structure, the surface As atoms each have two surface electrons while the Ga atoms each have two unfilled dangling bonds. Chelikowsky, Louie, and Cohen[5] recently performed a self-consistent pseudopotential calculation for an 11-layer slab of GaAs(110) with a rearranged surface. The surface states they obtained had qualitative features which were in much better agreement with the experimental data. In particular, their calculated As-derived surface-state peak at the valence-band maximum now broadened and moved to lower energies, in agreement with experiment. However, a significant discrepancy still exists: the threshold energy of the Ga-derived surface band is inside the band gap, contrary to experiments which show no empty surface states within the gap.

It is clear that an accurate theoretical determination of the surface electronic properties of the (110) face requires an accurate knowledge of the atomic geometry of the surface. In this paper we present the results of dynamical LEED calculations on the (110) face. We compare these calculations with our experimentally measured intensity-voltage (*I*-*V*) curves to determine the positions of the surface atoms. We also compare the structure obtained in this work with results of earlier calculations.

II. DATA COLLECTION

The crystals used in this work were 2.8×10^{18} cm^{-3} silicon-doped GaAs(110) wafers obtained from Laser Diode Laboratories, Inc. The crystals were mechanically polished, then mildly etched with a bromine-methanol solution. They were then placed in the vacuum system on a manipulator sample stage which could be indirectly heated to about 750 K or cooled to 95 K. After a bakeout of the vacuum system a base pressure of about 3×10^{-10} Torr was obtained. The sample was then cleaned by the standard procedure of ion bombardment (400-eV argon ions) and annealing (750 K for 1 h). This procedure resulted in surfaces which were well ordered as indicated by the sharp LEED spots, and which Auger analysis indicated were clean except for a trace (less than 1%) amount of carbon.

LEED *I*-*V* spectra were obtained for the first 16

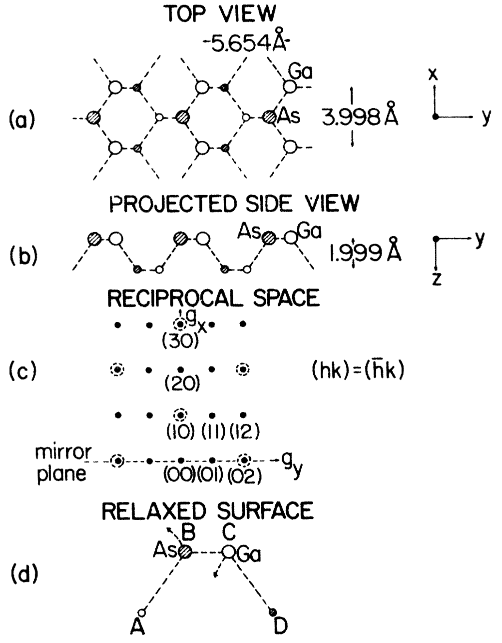

FIG. 1. Schematic diagrams of ideal (a), (b), and relaxed (d) structures of GaAs(110). Large circles denote surface atoms, small circles denote atoms in second atomic plane. The reciprocal-lattice beams circled in (c) are predicted to be weak for the ideal surface structure, but are not weak in a relaxed structure.

inequivalent nonspecular beams to emerge from the sample. The notation for these beams is shown in Fig. 1(c). The intensities of these diffracted beams were measured by the spot photometer technique and corrected for the energy dependence of the intensity of the incident electron beam. The first grid of the four-grid LEED optics was biased positively during these measurements so that the diffracted beams could be observed and measured at lower energies than would otherwise be possible. In order to reduce thermal effects, the sample temperature was maintained at 95 K during the measurements by flowing liquid nitrogen through the sample holder.

At least three other sets of GaAs(110) LEED I-V curves have been published. These include the data of MacRae and Gobeli[7,8] for the (01), (0$\bar{1}$), and (10) beams, the data of Lubinsky *et al.*[11] for the (0$\bar{1}$) and (10) beams, and the data of Duke *et al.*[12] for the (01) and (10) beams. The data obtained in this work are in general agreement with these previously published works for peak positions, but all four works are in substantial disagreement about relative peak intensities and peak shapes. We believe that the present data are the most useful in comparison to theoretical results, however, because thermal effects have been reduced, the data are obtained at lower energies, and many more beams are included.

It is well known that the silicon surface obtained immediately after cleavage shows a 2×1 reconstruction, but that after annealing it converts to either a 1×1 (at 360 °C) or 7×7 (at 400 °C) reconstruction, indicating that changes in the surface atomic structure have occurred. It might therefore be thought that the surfaces of our GaAs crystals prepared by ion bombardment and anneal have a different atomic structure than the surfaces of vacuum-cleaved GaAs which are generally used in photoemission studies. MacRae and Gobeli,[7] however, have shown that this is not the case for GaAs. In fact, they state that the LEED I-V curves obtained from vacuum-cleaved surfaces are identical to those from ion bombarded and annealed surfaces, except for a uniform decrease in peak intensities. Thus both methods of surface preparation produce samples with identical atomic structures.

III. COMPUTATIONAL DETAILS

Since the LEED pattern for the (110) surface shows no fractional order spots, the surface unit cell must contain only two atoms, as shown schematically in Fig. 1. The rearranged model calls for the As atoms in the surface layer to tilt outward and the Ga atoms to tilt inward [Fig. 1(d)]. As a result, the rearranged (110) surface may be viewed as either two closely spaced monatomic sublattices, one of As and one of Ga, or a diatomic layer with two noncoplanar atoms in the unit cell. In normal cases, it is easier computationally to adopt the former picture and use one of the K-space dynamical methods,[13] such as renormalized forward scattering (RFS) or layer doubling, for calculating the LEED I-V curves. However, in this case, the separation distance between the As and Ga sublattices in the rearranged surface can be very small (less than 0.4 Å). When this happens K-space methods become numerically unstable, partly because of the large number of beams needed for such small interplanar distances. We have therefore used a recently developed approach called the combined space method (CSM)[14] for calculating I-V curves of rearranged surface structures. This method is a dynamical computation scheme specifically constructed to treat closely spaced noncoplanar surface layers and avoids the numerical difficulties faced in K-space methods. Besides rearranged surface structures, the combined space method is also useful in analyzing hydrogen or other small overlayer atoms chemisorbed on metal surfaces. Inputs to the dynamical calculation included an inner potential of 10 eV, a uniform inelastic damping (imaginary potential) of 5 eV, and a temperature correction in terms of the Debye model of mean-square vibration amplitudes. Because the experimental data were obtained on a cold surface, the temperature correction in the theory is not very large ($T/\Theta_D \ll 1$). Phase shifts of GaAs were derived from self-consistent potentials constructed by Moruzzi *et al.*[15]

IV. DETERMINATION OF THE REARRANGED SURFACE STRUCTURE

I-V curves were first calculated for the ideal (110) surface structure. It was found that some of the beams which were calculated to be very weak [those shown in Fig. 1(c)] were experimentally quite strong. For the other beams large differences were found between the calculated curves and the experimental results. An example of these differences is shown in Fig. 2 for the (12) beam. We note at least five peaks in the experimental curve which are absent in the calculated curve. These discrepancies show that LEED intensity spectra are sensitive indicators of surface structure and indicate that the surface atoms on the (110) face of GaAs must be rearranged.

Since earlier models had suggested that the As atoms rotate outward and the Ga atoms rotate inward, we considered 11 relaxed surface structures which all had this general feature. These structures can be described by the combination of a rotation through an angle ω, and a change in the bond length of the surface atoms. We calculated *I-V* curves for relaxed structures with $\omega = 34.8°$, 27°, and 20°, where ω is measured in the plane AB_1C_1D, normal to the (110) plane, as shown in Fig. 3. If the surface bond length between As and Ga atoms is fixed at the bulk value, and $\omega = 34.8°$, then B_1C_1D is a straight line. This means the surface Ga atom and its three As nearest neighbors form a planar structure. This is the surface structure chosen by Duke *et al.*[11,12] on the basis of their LEED analysis (they chose $34.8° \geq \omega \geq 27°$, but stated a preference for the 34.8° value). We studied the same atomic rearrangement and concluded that it is not the correct structure for the (110) surface. The distance $d_\perp$ (i.e., the height of C_1 above the line AD) for $\omega = 34.8°$ is 1.396 Å, if the bond length is kept at 2.448 Å (bulk value). Besides this structure, we considered changing $d_\perp$ to 1.296 and 1.496 Å, structures obtained by rigidly displacing B_1 and C_1 towards and away from AD, respectively, keeping the angle ω unchanged. The former displacement shortens the As and Ga back bonds (i.e., lengths AB_1 and DC_1), while the latter elongates both back bonds. For a rotation angle of $\omega = 27°$, we considered five possibilities which correspond to placing the surface Ga atom at locations C_1, C_2, ..., C_5. The values of $d_\perp$ for the five structures are 1.552, 1.452, 1.352, 1.352, and 1.111 Å, respectively. The last structure, $d_\perp = 1.111$ Å, corre-

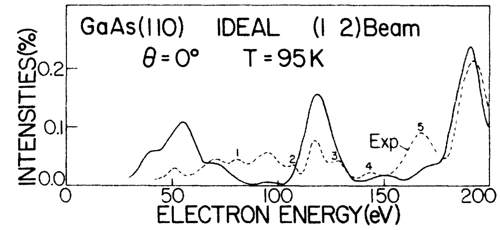

FIG. 2. Comparison of calculated *I-V* curve for the (12) beam with experiment. Peaks numbered are either missing or very small in the calculated curve.

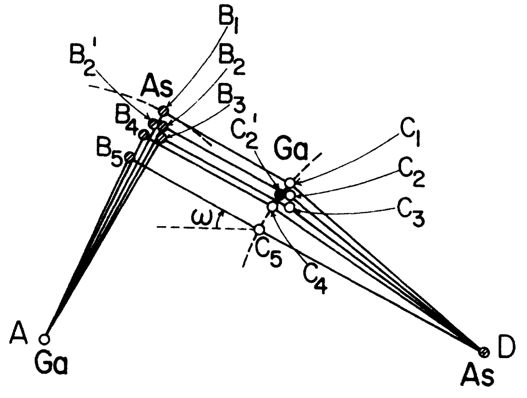

FIG. 3. Projected side view of relaxed models for GaAs(110). The lengths B_1C_1, B_2C_2, $B_2'C_2'$, ..., etc. are all the same.

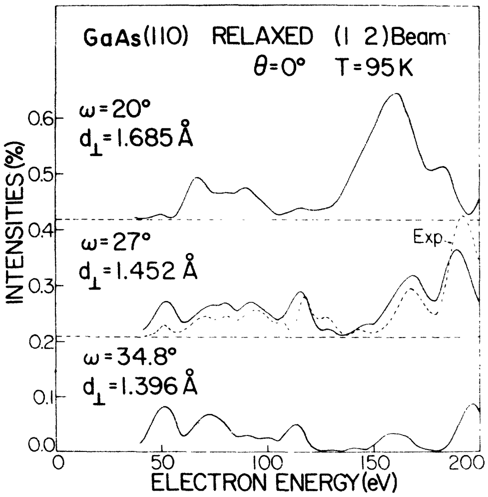

FIG. 4. The calculated *I-V* curves for the (12) beam corresponding to different relaxed models are compared with experiment.

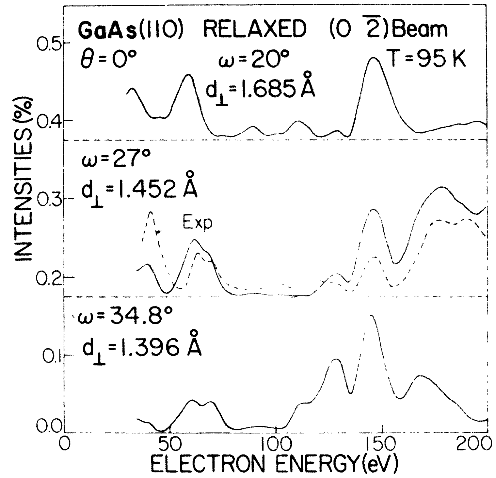

FIG. 5. Same as in Fig. 4, except for the $(0\bar{2})$ beam. The $(0\bar{2})$ beam is predicted by the ideal surface structure to be very weak. It is not weak in the relaxed models or experiment.

sponds to points B_5C_5D falling on a straight line. Structures C_4 and C_5 shorten the surface As back bond, keeping the Ga back bond fixed in length. Structures C_2 and C_3 shorten both As and Ga back bonds. For $\omega = 20°$, we considered three surface arrangements. The first corresponds to keeping the bond length identical to the bulk value. In this case, $d_\perp$ is 1.685 Å. We then displace the surface atoms towards AD, causing the As and Ga back bonds to contract, but keeping ω and the length at the surface B_1C_1 fixed. The values of $d_\perp$ in these structures are 1.535 and 1.385 Å.

Intensity-voltage curves were calculated for the 11 surface models. It is useful to establish the degree of sensitivity of the I-V curves to various displacements of the surface Ga and As atoms.

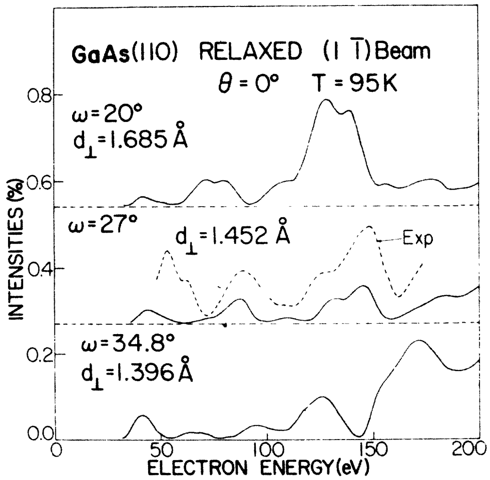

FIG. 6. Same as in Fig. 4, except for the $(1\bar{1})$ beam.

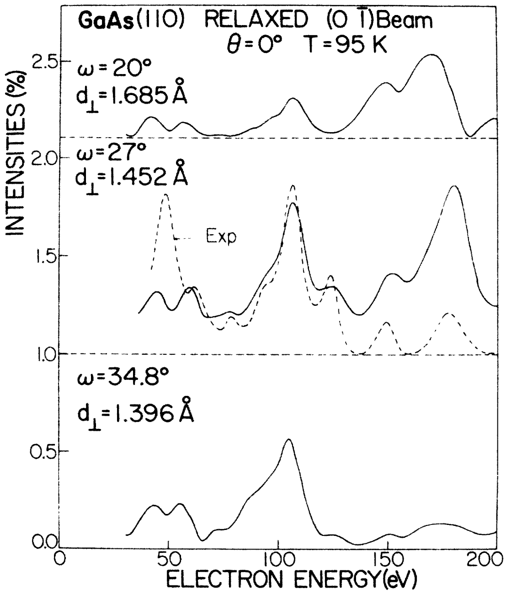

FIG. 7. Same as in Fig. 4, except for the $(0\bar{1})$ beam.

Figures 4–10 show the comparison between theory and experiment for several reflected beams for three of the structures: $\omega = 34.8°$, $d_\perp = 1.396$ Å, $\omega = 27°$, $d_\perp = 1.452$ Å, and $\omega = 20°$, $d_\perp = 1.685$ Å. There are clearly large differences between the calculated curves. The surface structure corresponding to C_2 in Fig. 3 ($\omega = 27°$, $d_\perp = 1.452$ Å) is the one we judged to give the best agreement between theory and experiment. The structure with $\omega = 34.8°$, $d_\perp = 1.396$ Å, previously picked by Duke *et al.* in Refs. 11 and 12, shows much worse agreement, as does the structure with $\omega = 20°$. In the calculation of Duke

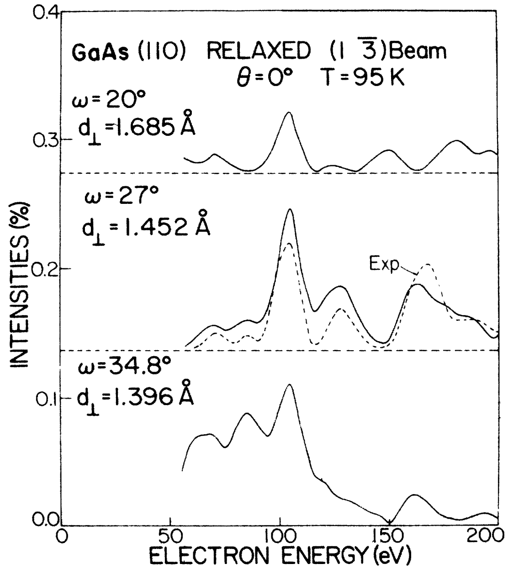

FIG. 8. Same as in Fig. 4, except for the $(1\bar{3})$ beam.

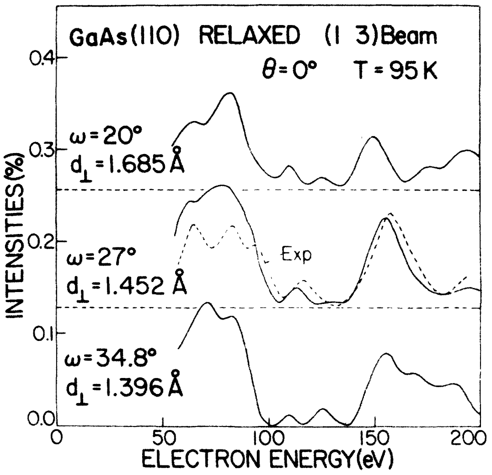

FIG. 9. Same as in Fig. 4, except for the (13) beam.

et al.[11,12] for the relaxed structure, interlayer multiple scatterings between the relaxed surface layer and deeper bulklike layers were not done accurately. As a result, they were unable to obtain the same degree of agreement between theory and experiment as in this work. Apparently, this inaccuracy also affected the value of ω that was determined.

In addition to the angle of rotation, the I-V curves are also sensitive to the value of the interlayer spacing $d_\perp$. Figure 11 shows the variation in calculated curves as $d_\perp$ is changed. The sensitive response of I-V curves to $d_\perp$ means the heights of the surface atoms above the second layer may be accurately determined. The I-V curves, however, are not very sensitive to lateral shifts of the surface atoms parallel to the (110) surface. For example, the I-V curves calculated for structures C_3 and C_4, which differ only by a rigid lateral shift of 0.15 Å, disagree only by rather minor movements of peak shoulders and changes in peak heights. An example of this is shown in Fig. 12. Such changes in the calculated I-V curves do not provide enough evidence for an unambiguous determination of small lateral shifts of surface atoms.

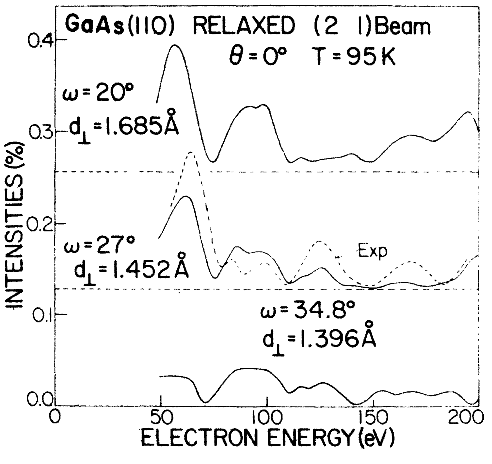

FIG. 10. Same as in Fig. 4, except for the (21) beam.

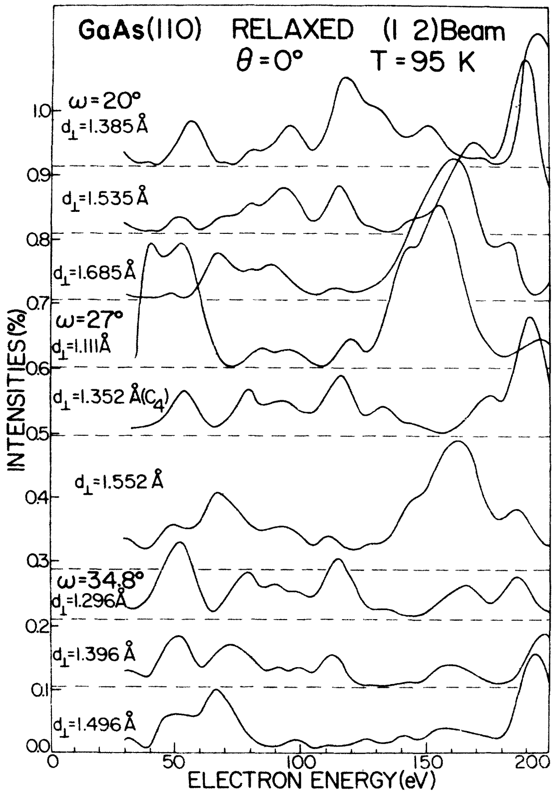

FIG. 11. Calculated I-V curves for the (12) beam corresponding to different $d_\perp$ spacings and relaxed structures.

V. COMPARISON WITH PREVIOUS RESULTS AND CONCLUSION

In Sec. IV, we established that LEED I-V curves are sensitive to the tilt angle and to vertical heights

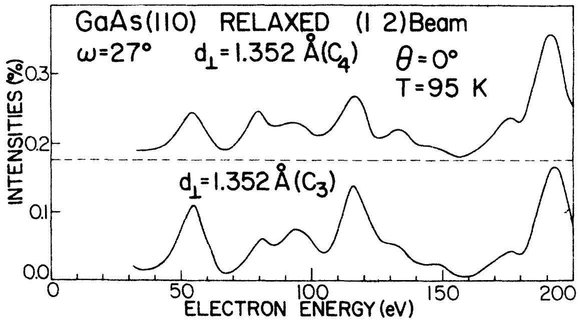

FIG. 12. Calculated I-V curves for the (12) beam corresponding to structures with laterally shifted surface atoms parallel to the (110) surface.

of the surface atoms from the second layer, but are not sensitive to lateral shifts (≤ 0.2 Å) of the surface atoms. The relaxed structure which we found to give the best agreement with experiment is $\omega = 27°$ and $d_\perp = 1.452$ Å. If the surface-bond length in the relaxed layer is set equal to the bulk value, then this structure indicates a contraction of 0.09 Å or 3.6% in the surface As back bond (i.e., AB_2). The surface Ga back bond (i.e., length C_2D) is contracted by a lesser amount, 0.06 Å or 2.5%. On the other hand, one may shift the surface Ga atom laterally from C_2 to C_2 (Fig. 3), and the As atom from B_2 to B_2. This shift would mean zero contraction in the Ga back bond and a contraction in the As back bond of 0.12 Å or 5%. Since LEED analysis of I-V curves is at present not accurate enough to select unambiguously between such laterally shifted structures, we conclude that in terms of surface bond lengths, the Ga back bond (C_2D) is contracted probably by no more than 2.5%. The surface As back bond is contracted by about 3.6% or perhaps more. So far, we have kept the surface bond length B_2C_2 in the relaxed layer fixed. If this length is allowed to contract, the surface Ga back bond could actually elongate, while the surface As back bond would contract.

From results of photoemission measurements on the (110) surface, it is believed that the surface As atoms have two surface electrons, whereas the Ga atoms have lost their surface electrons. The concentration of electron charge at B_2 could lead to bond length contraction along AB_2. On the other hand, the depletion of the surface dangling electron at the Ga atom (C_2) could lead to a bond length conservation or elongation along C_2D. This picture is generally consistent with the surface structure we have determined, i.e., the major distortion of bond distance is in the As surface back bond along AB_2, which is contracted. The bond lengths C_2D and B_2C_2 undergo (undetermined) lesser changes.

Duke *et al.*,[16,17] have recently made kinematical (single scattering) calculations of LEED intensities on the GaAs(110) surface. By comparing the results of these calculations with their experimental data, they have determined two new surface structures. These structures are characterized by $\omega = 23°$ and $d_\perp = 1.60$ Å, and by $\omega = 17.7°$ and $d_\perp = 1.25$ Å. The first of these new structures, termed "best" in the analysis,[17] corresponds to a surface As back bond elongation of 0.17 Å or 6.8% and a Ga back bond contraction of 0.31 Å or 12.8%. The second surface structure, termed ionic in the analysis, corresponds to an As back bond contraction of 0.24 Å or 9.8% and Ga back bond contraction of as much as 0.56 Å or 23%. In each case, their surface models have the Ga back bond *contracted* more than the As back bond, a trend contrary to the results of this study.

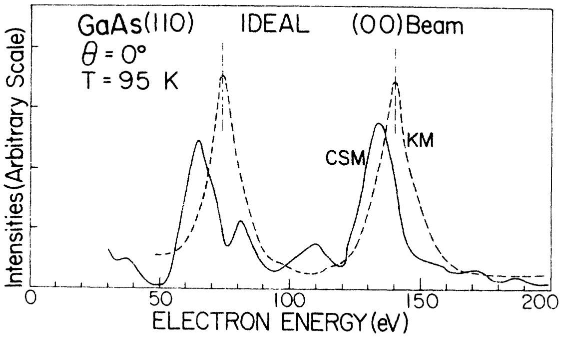

FIG. 13. Comparison between kinematical and dynamical (combined space method) results for the (00) beam.

We have investigated the applicability of the kinematical method to LEED calculations on various faces of GaAs, including the (110) face. Our findings[18] indicate that such calculations give erroneous positions of major peaks by nonuniform amounts of as much as 10 eV. As a result, we concluded that kinematical I-V curves are unreliable and therefore useless as an aid in determining the correct surface structure for this compound. As an example of the erroneous results of kinematical calculations on GaAs(110), we show in Figs. 13 and 14 I-V curves for the unrearranged (110) surface obtained using a kinematical model and the combined space method. Both calculations used an inner potential of 10 eV. As expected, I-V curves from the kinematical calculation do not contain any secondary peaks. The major difficulty, however, is that "Bragg" peaks are placed at the wrong energies [e.g., shifts of Bragg peaks in the (00) beam are 9 and 6 eV, shifts in the (12) beam are 8, 3, and 7 eV]. Similar nonuniform shifts in Bragg peak energy positions occur for every reflected beam. Because the peak energy shifts are nonuniform, they cannot be corrected by a constant inner potential difference. These errors in calculated peak positions are bound to create errors in the determined surface structures.

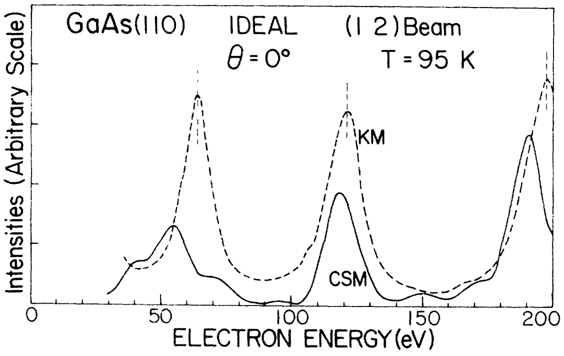

FIG. 14. Same as in Fig. 13, except for the (12) beam.

To conclude, our work supports a surface model in which the angle of rotation ω is 27° and the major bond length distortion is a contraction in the surface As back bond. Further determination by LEED of other bond-length changes requires more accurate knowledge of the surface-scattering potential and inelastic damping.

As an added note, Pendey, Freeouf, and Eastman[19] recently carried out a tight-binding calculation of electronic distribution on the GaAs(110) surface for various relaxed surface structures. Comparing the local density of states (LDS) with ultraviolet photoemission data,[20] they arrived at a similar conclusion that the correct tilt angle ω must be *less* than 34.8°. Unfortunately, the LDS is not very sensitive to the exact value of ω and their determined value of 19° is smaller than that reported in this work. However, their main conclusion agrees with our result that 34.8° is too large. Since LEED I-V curves are sensitive to ω, but not to lateral shifts of surface atoms of $\lesssim 0.2$ Å, it is hoped that some other surface technique, perhaps angle-resolved ultraviolet photoemission, can in the future provide a more detailed determination of the various bond lengths of the relaxed (110) surface.

ACKNOWLEDGMENT

One of us (S.Y.T.) was supported in part by NSF Contract No. DMR 73-02614.

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