Semiconductor Surface Reconstruction: The Rippled Geometry of GaAs(110)

A. R. Lubinsky and C. B. Duke

Webster Research Center, Xerox Corporation, 800 Phillips Road, Webster, New York 14580

and

B. W. Lee and P. Mark*

Department of Electrical Engineering, Princeton University, Princeton, New Jersey 08540

(Received 24 December 1975)

Extension of analyses of low-energy-electron-diffraction intensities to encompass structure determination of low-index semiconductor surfaces reveals that GaAs(110) is reconstructed. The As atoms protrude from the surface whereas the Ga atoms are displaced inward such that no nearest-neighbor bond lengths are altered.

Although much recent attention has been focused on determinations of the electronic structure of polar semiconductor surfaces by photoemission[1-5] and electron-energy-loss[6,7] spectroscopy, detailed interpretation of the resulting spectra has been delayed by ignorance of the atomic geometry of these surfaces. In this Letter we employ an extension of our earlier elastic low-energy-electron-diffraction (ELEED) intensity analyses[8,9] to determine the atomic geometry of the cleavage plane of GaAs [GaAs(110)]. The resulting structure is interesting because it is a distortion of the bulk geometry of (110) planes which can be interpreted as a direct consequence of the nature of chemical bonding in molecules of group-III and -V elements. Thus, we demonstrate herein the feasibility of using ELEED intensity analysis to determine the atomic geometry of subtly reconstructed semiconductor surfaces: a long anticipated[8] but heretofore unrealized application of the dynamical theory of ELEED, analogous to recent advances in its application to adsorbed overlayers.[10,11]

GaAs platelet crystals with (110) large-area surfaces were purchased from the Laser Diode Corporation and chemically polished.[12] They were mounted in Mo foil in a metal sample holder suitable for resistive heating. The ELEED intensities and Auger-electron spectra of the resulting GaAs(110) surfaces were monitored[13] during cycles of simultaneous argon ion bombardment and annealing until reproducible ELEED intensities were obtained in the absence of detectable concentrations of surface contaminants. The final ELEED intensity profiles were taken at room temperature using a spot photometer. The observed spot pattern, indicated in Fig. 1, is characteristic of a truncated bulk zinc-blende lattice, revealing that surface reconstruction of

GaAs(110) can be detected only via quantitative analysis of the ELEED intensities.[14]

Such an analysis was carried out using a multiple-scattering computer program[9] in which electron diffraction from the uppermost two atomic layers was evaluated exactly[8] whereas that from deeper layers was approximated by use of the layer-iteration method.[15,16] A muffin-tin-potential calculated from the charge density of Ga^+ and As^- species was utilized to evaluate their atomic scattering factors. Direct evaluation of the resulting differential scattering cross sections revealed that for $E \leqslant 150$ eV, six phase
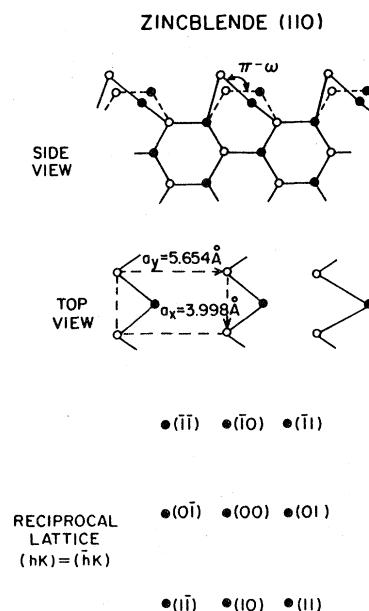

FIG. 1. Schematic indication of the surface atomic geometry and the associated ELEED normal-incidence spot pattern (i.e., reciprocal lattice) for the (110) surface of a zinc-blende crystal like GaAs. The bond-rotation angle, ω, is shown in the upper panel.

shifts suffice to describe these cross sections. Hence, the first six phase shifts, an inner potential of 8 eV, and an inelastic-collision penetration depth of 8 Å were utilized in the multiple-scattering calculations.

Our structure analysis was performed by evaluating the model ELEED intensities for a series of hypothetical surface geometries and comparing them with the observed intensities to decide upon the most probable atomic geometry. Three criteria were utilized to perform this selection: the description of the observed line shapes in the intensity profiles, the prediction of the relative intensities of the various beams, and the reproduction of prominent maxima in the intensity profiles to within 3 eV.

While it is obvious that not all atomic geometries can be examined, previous considerations[7,14,17,18] of possible geometries for GaAs(110)

plus elementary symmetry and chemical considerations (e.g., the incompressibility of bonds) permit considerable reductions in the range of structures considered. In particular, we examined the consequences of variations in the uppermost layer spacings (equal to 2.0 Å in the bulk) and of bond rotations as proposed initially by Levine and Freeman,[17] and indicated schematically in the upper panel of Fig. 1. Comparison of the calculated and observed intensity profiles is shown in Figs. 2 and 3 for typical beams which are strong in the absence of reconstruction. In contrast to the $(0\bar{1})$ and (01) beams considered in Figs. 2 and 3, however, the (10) and $(\bar{1}0)$ beams would be very weak in the absence of surface reconstruction, vanishing if the Ga and As electron scattering factors were equal. Experimentally the (01) and (10) beams are of comparable intensity, a fact leading to the original suggestion[14]
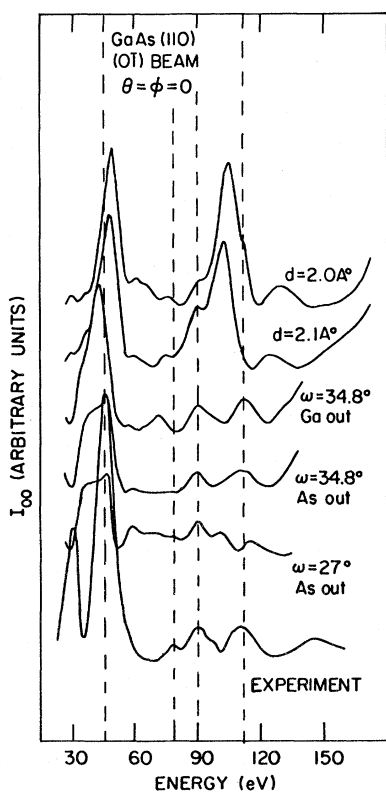

FIG. 2. Comparison of calculated and measured ELEED intensities for the $(0\bar{1})$ diffracted beam associated with electrons normally incident on GaAs. The upper curve was obtained using the truncated bulk geometry, that below it an expanded upper-layer spacing, and the next three lower ones bond rotations of the sort shown in Fig. 1. The observed intensities are presented in the lower curve. Vertical dashed lines through observed maxima are for illustrative purposes.
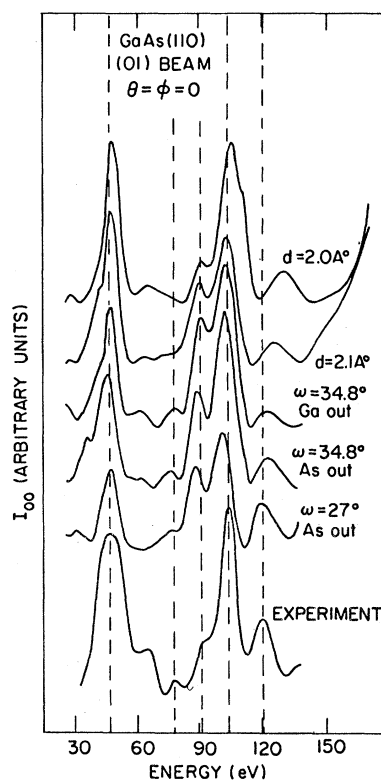
FIG. 3. Comparison of calculated and measured ELEED intensities for the (01) diffracted beam associated with electrons normally incident on GaAs. The upper curve was obtained using the truncated bulk geometry, that below it an expanded upper-layer spacing, and the next three lower ones bond rotations of the sort shown in Fig. 1. The observed intensitites are presented in the lower curve. Vertical dashed lines through observed maxima are for illustrative purposes.
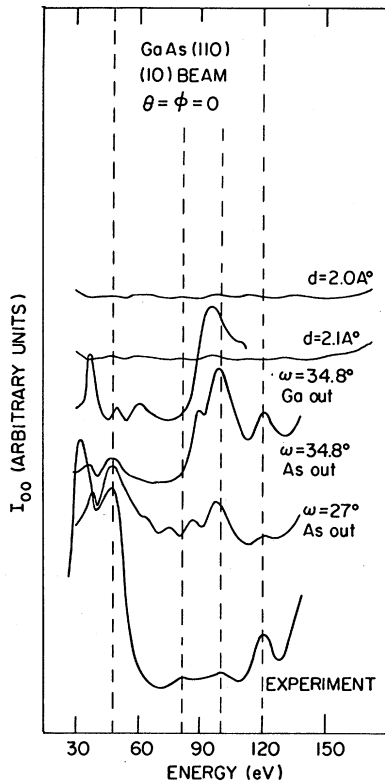
FIG. 4. Comparison of calculated and measured ELEED intensities for $(10) = (\bar{1}0)$ diffracted beam associated with electrons normally incident on GaAs. The upper curve was obtained using the truncated bulk geometry, that below it an expanded upper-layer spacing, and the next three lower ones bond rotations of the sort shown in Fig. 1. The observed intensities are presented in the lower curve. Vertical dashed lines through observed maxima are for illustrative purposes.

that (110) faces of III-V semiconductors might be reconstructed. The bond-rotation structure yields comparable intensities for these beams, with the comparison between the observed and calculated intensity profiles shown in Fig. 4. Whereas the $(0\bar{1})$ and (01) beams do not discriminate rotations in which the Ga moves outward from those in which the As moves outward, the (10) beam reveals clearly that the latter is more probable.

The generally satisfactory agreement in both line shape and magnitude of the calculated and observed ELEED inensities for the bond-rotation geometry leads us to conclude that the As atoms are rotated out of the (110) surface plane and Ga atoms inward from this plane by $34.8° \leqslant \omega \leqslant 27°$. Statistically, the larger rotation angles are preferred with the (maximum possible) rotation angle of $\omega = 34.8°$ predicting to within 3 eV some 80%

of the observed ELEED intensity peaks (five beams, 26 peaks) whereas $\omega = 27°$ leads to a correct prediction of only 70% of these maxima. As evident from the figures, nonrotated surface geometries yield such poor descriptions of the ELEED intensity data (predicting to within 3 eV only about 40% of the observed peaks) that they cannot be considered as serious candidates for the correct structure. Therefore, whereas more extensive data and analysis could lend to further refinement of the structure, our results reveal that a wavelike or "rippled" geometry consisting of planar or nearly planar As-Ga-As wave fronts parallel to the $(1\bar{1}0)$ directions in the surface is a good first approximation to this structure, accurate to within distances of about 0.1 Å.

In summary, we believe that our ELEED intensity analysis provides convincing confirmation that the GaAs(110) surface is reconstructed. The Ga species rotate inward to an approximately planar, threefold coordination with its As nearest neighbors whereas the uppermost As species moves outward into a corresponding pyramidal configuration with its three Ga neighbors. The apex of this pyramid is constrained by the requirement that the Ga-As bond lengths not change appreciably from those characteristic of the bulk. Thus, the surface configuration is analogous to that of the corresponding hydrides, with the extra "lone-pair" charge density on the As being directed normal to the base of the pyramid of Ga atoms to which it bonds.[19] Furthermore, the uppermost occupied orbital associated with the $AsGa_3$ pyramidal complex is completely filled, leading to the absence of any further tendency to surface reconstruction via Peierls (or Jahn-Teller) instability. The fact that the lone-pair charge density lies on As rather than Ga is responsible for the As protruding upward. The Coulomb energy between the lone-pair and bonding charge densities is thereby minimized. Since Ga has no lone-pair charge density, its bonding Coulomb energy is minimized by a sp^2 planar configuration. Therefore the reconstructed surface geometry of GaAs(110) can be understood in terms of the Ga and As surface species relaxing to the chemically appropriate threefold rather than fourfold coordinated positions once the constraint imposed by the bulk tetrahedral bonding is removed by cleavage.

nedy for her assistance.

[1]D. E. Eastman and W. D. Grobman, Phys. Rev. Lett. 28, 1378 (1972).

[2]P. E. Gregory, W. E. Spicer, S. Ciraci, and W. A. Harrison, Appl. Phys. Lett. 25, 511 (1974).

[3]D. E. Eastman and J. L. Freeouf, Phys. Rev. Lett. 33, 1601 (1974), and 34, 1624 (1975).

[4]G. J. Lapeyre and J. Anderson, Phys. Rev. Lett. 35, 117 (1975).

[5]P. Pianetta, I. Lindau, C. Garner, and W. E. Spicer, Phys. Rev. Lett. 35, 1356 (1975).

[6]R. Ludeke and A. Koma, Phys. Rev. Lett. 34, 817 (1975); R. Ludeke and L. Esaki, Phys. Rev. Lett. 33, 653 (1974).

[7]J. E. Rowe, S. B. Christman, and G. Margaritondo, Phys. Rev. Lett. 35, 1471 (1975).

[8]C. B. Duke, Adv. Chem. Phys. 27, 1 (1974), and in Proceedings of the International School of Physics "Enrico Fermi," Course LVIII, edited by F. O. Goodman (Editorice Compositori, Bologna, 1975), pp. 99-213.

[9]C. B. Duke and A. R. Lubinsky, Surf. Sci. 50, 605 (1975); A. R. Lubinsky, C. B. Duke, S. C. Chang, B. W. Lee, and P. Mark, to be published.

[10]S. Y. Tong, Prog. Surf. Sci. 7, 1 (1975).

[11]P. M. Marcus, J. E. Demuth, and D. W. Jepsen, Surf. Sci. 53, 501 (1975).

[12]J. D. Levine, unpublished. We are indebted to Dr. Levine for preparing the surfaces for us at the RCA Laboratories in Princeton, N. J.

[13]S. C. Chang and P. Mark, Surf. Sci. 45, 721 (1974), and 46, 293 (1974).

[14]A. U. MacRae and G. W. Gobeli, J. Appl. Phys. 35, 1629 (1964).

[15]J. B. Pendry, Phys. Rev. Lett. 27, 856 (1971).

[16]S. Y. Tong, Solid State Commun. 16, 91 (1975).

[17]J. D. Levine and S. Freeman, Phys. Rev. B 2, 3255 (1970).

[18]W. E. Spicer, P. W. Chye, P. E. Gregory, T. Sukegawa, and I. A. Babalola, to be published.

[19]A. W. Potts and W. C. Price, Proc. Roy. Soc. London, Ser. A 326, 181 (1972).

Magnetic Structure of an Amorphous Rare-Earth Transition-Metal Alloy

J. M. D. Coey

Groupe des Transitions de Phases, Centre National de la Recherche Scientifique, 38042-Grenoble-Cedex, France

and

J. Chappert

Groupe Interactions Hyperfines, Centre d'Etudes Nucléaires, 38041-Grenoble-Cedex, France

and

J. P. Rebouillat and T. S. Wang*

Laboratoire de Magnétisme, Centre National de la Recherche Scientifique, 38042-Grenoble-Cedex, France

(Received 16 December 1975)

^{161}Dy Mössbauer spectra show that the dysprosium moments in amorphous $DyCo_{3.4}$ are strongly coupled to the local crystal field axes. The magnetic structure is one in which the cobalt "sublattice" is strongly ferromagnetic, and the dysprosium moments are almost randomly distributed in directions between antiparallel and perpendicular to the cobalt.

Although ferromagnetism in amorphous alloys is well known,[1] the rich variety of more complex magnetic structures which can occur in amorphous solids is just now becoming apparent. Amorphous rare-earth transition-metal alloys in particular are much studied at present.[2-6] The magnetic structures in these alloys will be strongly influenced by the local anisotropy field at the rare-earth sites, just as in their crystalline counterparts. Harris, Plischke, and Zuckermann[7] have suggested that this field, determined by the spatial configuration of the neighboring atoms, will be random in direction and comparable in magnitude to the exchange field experienced by the rare-earth ions. In this Letter we present direct evidence that the directions of the rare-earth moments are closely correlated with the directions of the local anisotropy field in amorphous $DyCo_{3.4}$. The magnetic structure [Fig. 3(b)] is deduced from Mössbauer spectra and magnetization measurements. Finally we outline a classification scheme for magnetic order in