PHYSICAL REVIEW B VOLUME 41, NUMBER 8 15 MARCH 1990-I

Growth of bismuth films on GaAs(110) studied using low-energy electron diffraction

T. Guo, R. E. Atkinson, and W. K. Ford
Advanced Materials Center and the Department of Physics, Montana State University, Bozeman, Montana 59717

(Received 18 September 1989; revised manuscript received 30 October 1989)

The growth of bismuth films on GaAs(110) has been studied with use of low-energy electron diffraction. The overlayer forms epitaxially in the first monolayer, two dimensionally disordered in the second, and three dimensionally at higher coverages. Below 1 monolayer an attractive interchain force directed perpendicular to the chain direction governs island formation. A (6×1) reconstruction at 1 monolayer confirms that the 24-Å average chain length revealed previously by scanning tunneling microscopy is part of the long-range surface order and is not indicative of an incommensurate overlayer.

INTRODUCTION

Metals are not generally known to form ordered overlayers on the low-index surfaces of III-V compound semiconductors.[1,2] This is true not only for the industrially important, albeit complex (100) surfaces, but also for the (110) surface which is comparatively simple and scientifically well understood. Nevertheless, there is deemed great importance in being able to create microscopically ordered metal-semiconductor interfaces for the development of improved Ohmic contacts and of controllabe Schottky-barrier-height devices,[1] particularly for the (100) interfaces. The attainment of this goal can only occur by understanding more clearly the nature of the chemical bonding at the interface between metallic atom and semiconductor substrate. To this end one must answer how and to what extent the metallic adatom bond can be made to conform to the substrate system, with its directed covalent bonds, and to do so uniformly over the breadth of the interface region. In turn, this will allow one to predict under what growth conditions an epitaxial overlayer will form and what factors determine those conditions. At present the study of the microscopic factors that drive epitaxy is best done for model systems on the experimentally tractable (110) surfaces, for which the substrate atomic reconstructions are well known,[2] and quantitative theoretical models for both the surface reconstruction and the surface electronic structure are available.[3] Notwithstanding, the formation of ordered metallic contacts remains a problem on this surface, the solution of which would assist in understanding the problems of interface formation for the general surface.

Two semimetals, antimony and bismuth, are valuable counter examples of the general rule. Antimony has been shown to form epitaxial overlayers on GaAs(110) and InP(110).[4,5] More recently, bismuth has been established to form epitaxial overlayers on GaAs(110),[6,7] GaSb(110), and InSb(110).[8] Bismuth is particularly interesting since, unlike antimony, it does not form tetrahedrally bonded compounds. Hence, it may better reflect the general problems associated with the formation of the metal-semiconductor interface. Experimental studies using this adatom should help to test more thoroughly the extant theoretical models of epitaxy and interface formation.

The growth of antimony films on GaAs(110) has been studied by numerous groups using various techniques.[9] It grows in a Stranski-Krastanov mode, with the first layer being epitaxial and subsequent layers forming a three-dimensionally disordered film. The conclusions of the present study is that bismuth growth is also Stranski-Krastanov. However, the first layer is epitaxial, the second layer is two-dimensionally disordered, and three-dimensional disorder begins with the third layer. The atoms of the first layer form as chains on the (110) substrate, but the chains have a characteristic length imposed probably by a lattice mismatch with the substrate. This introduces a weak, six-unit-cell periodicity in the surface potential along the $[1\bar{1}0]$ chain axis. At submonolayer coverages two-dimensional islanding occurs, but the dominant attractive force between chains is directed perpendicular to the chain axis, along the [001] crystallographic direction.

EXPERIMENTAL DETAILS

Quantitative low-energy electron diffraction (LEED) was used in this experiment to study the growth of bismuth films on GaAs(110). Both diffraction-beam-intensity–electron-energy measurements, or *I-V* curves, and diffraction spot profiling were performed at normal incidence using a newly developed video LEED diffractometer.[10] The surfaces were prepared from cleaved GaAs(110) Si-doped *n*-type bars having a carrier concentration of $(1.4\text{–}4)\times10^{18}$ cm^{-3}. Bismuth and antimony films were deposited by sublimation from the bulk at an evaporation pressure of less than 5×10^{-10} Torr and at a typical rate of less than 1 Å/min. Film deposition was monitored with a quartz-crystal oscillator (QCO) using the same calibration as used previously for photoemission measurements.[6] Several samples were checked by Rutherford backscattering which determined that the QCO was accurate to within approximately ±10%. Sample cleanliness was verified using Auger-electron spectroscopy. Samples could be cooled to a temperature of approximately 120 K and heated to a temperature in excess of 250 °C.

The instrumentation response function can be estimated using data from a cleaved GaAs(110) surface. First, the ratio of the full width at half maximum (FWHM) of the sharpest diffraction spot observed at a 130-eV incident-beam energy divided by the reciprocal-lattice constant was determined to be 0.047. Using the development of Lu and Lagally,[11] the FWHM of the instrument response function for this ratio is 0.53°. The corresponding transfer width of the system, defined by Park *et al.*,[12] is 119 Å. From the FWHM of the instrument response function we estimate the resolving capacity, or minimum angle of resolution,[11] of our instrument to be 0.33°, where a measurement uncertainty of 10% is assumed. Since the cleaved GaAs(110) surface is by no means perfect and the measurement error can be reduced, e.g., by integrating the picture over more frames, the actual FWHM of the response function and the minimum angle of resolution should be smaller than these estimates.

RESULTS

Electron-diffraction spot profiles were used to learn about the degree and character of the long-range order of the surface. Spot profiles were measured at several bismuth coverages and surface preparations. In Fig. 1 the contour profile of the $(0\bar{1})$ diffraction beam is presented at six energies for a surface covered with 0.4 monolayer of bismuth. This overlayer was prepared at room temperature and not annealed. The variation in the angular width of the diffraction beam varies with electron energy at this submonolayer coverage. No size variation occurs at coverages greater than or equal to 1 monolayer. Similar results were obtained for the antimony films studied.

A measure of the effect of annealing on surface order is presented in Fig. 2. In this figure the (01) diffraction beam from a surface covered by 0.7 monolayer of bismuth deposited at room temperature is depicted. The diffraction beams of the as-deposited films were diffuse at this coverage. The contour plot in panel (a) corresponds to the as-prepared surface and that in panel (b) reflects the effect of annealing this film to approximately 250 °C and then cooled. Both profiles were measured at room temperature. For this coverage no adatoms were expected to be desorbed at this annealing temperature because previous thermal desorption data established that the desorption temperature for the last monolayer of bismuth on GaAs(110) is 350 °C.[6] Analogous behavior to that observed in Fig. 2 was also observed for the other diffraction beams at this coverage.

Annealing had a similar effect as that represented in Fig. 2 on the spot profiles at all coverages up to 1 monolayer and little effect at coverages between 1 and 2 monolayers for either bismuth or antimony adlayers. The *I-V* curves also did not show significant changes when 1- and 2-monolayer films of either semimetal were annealed at high temperatures. This is interesting since the work of Schäffler *et al.*[13] suggested that annealing a 1-monolayer antimony film on *p*-type GaAs(110) near 300 °C reduces the photoemission linewidths, which was interpreted as indicating better ordering in the overlayer. In turn, changes observed in the degree of band bending when samples were annealed was ascribed to the perfection of ordering and elimination of extrinsic surface states. No manifestations of this effect was observed in the present LEED study. This supports the proposal of Cao *et al.*[14] that the formation of *p*-type surface defects were, instead, the cause of band-bending variations induced by annealing.

Figure 3 is a contour plot of the LEED profiles for several diffraction beams taken at 130 eV and at a sample temperature of approximately 150 K. This surface contained 1 monolayer of bismuth deposited at room temperature and was annealed at 250 °C for 20 min. In the figure the rectangular pattern of compact spots are due to the (1×1) integral-order diffraction. The unlabeled $(0\bar{1})$ beam has nearly zero diffraction intensity at this energy. Also apparent in the figure are two more diffuse sixth-order satellite spots split from the (11) and $(\bar{1}\,\bar{1})$ beams. Generally, sixth-order spots were observed near all

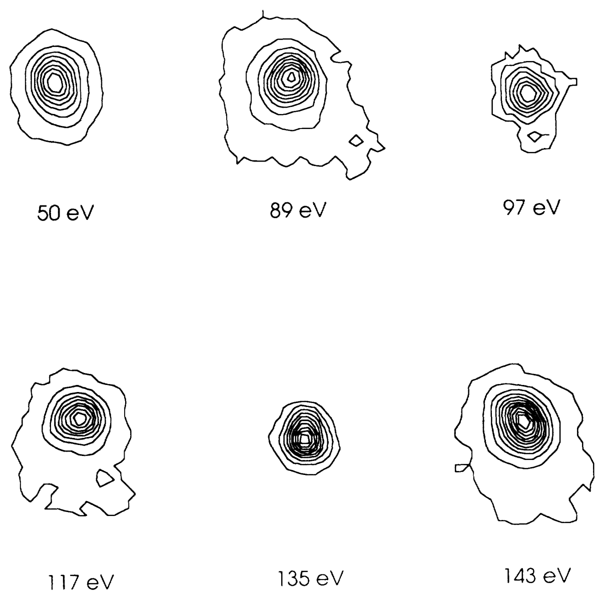

FIG. 1. Size effect on the $(0\bar{1})$ diffraction beam from a 0.4-monolayer bismuth film on GaAs(110).

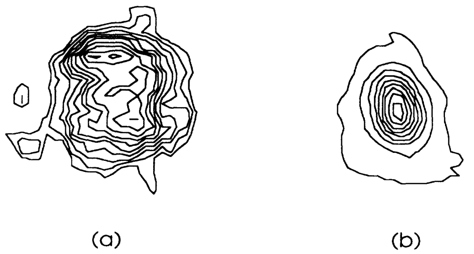

FIG. 2. Effect of annealing to 200 °C on the (01) diffraction beam at 89 eV from a 0.7-monolayer bismuth film on GaAs(110). The angular FWHM of the beam is ~2°.

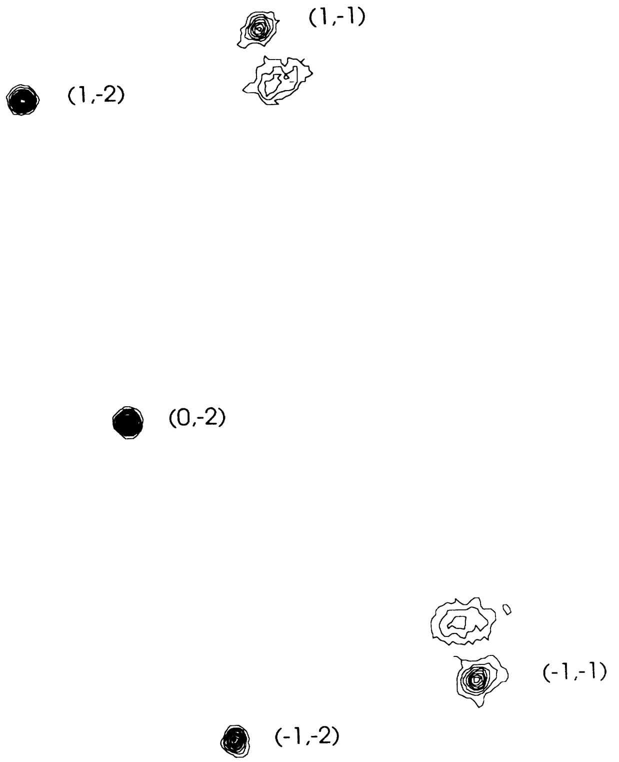

FIG. 3. LEED profiles at 130 eV for a 1-monolayer bismuth film on GaAs(110) at 150 K show presence of sixth-order spots.

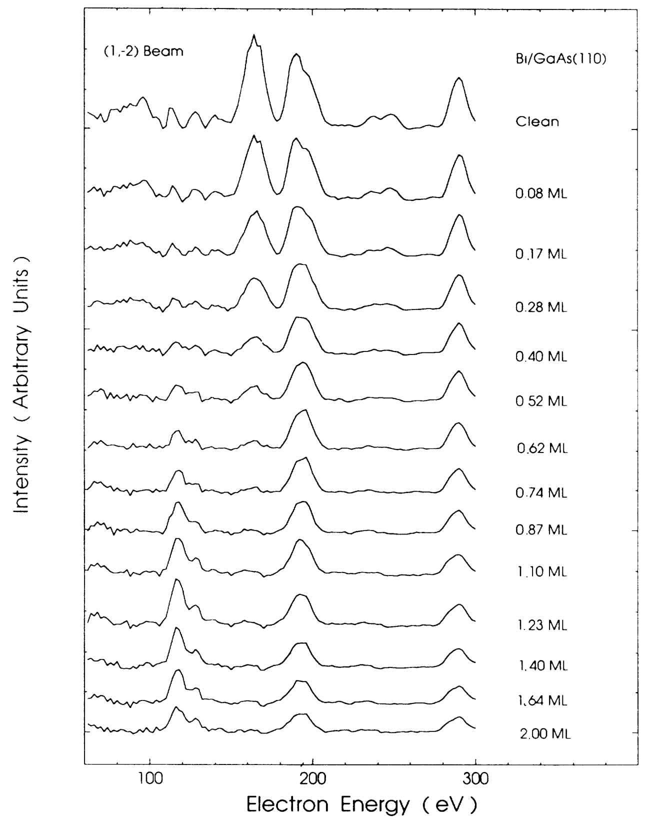

FIG. 4. Variation in the $(1\bar{2})$ diffraction beam with bismuth overlayer coverage.

integral-order spots with intensities that varied with electron gun energy. There was little evidence of the sixth-order spots at coverages below 0.7 monolayer, although the sixth-order spots were detected at least up to coverages of 2 monolayers. An ordering temperature near $-30\,^{\circ}\mathrm{C}$ has been determined by studying films prepared at low temperature and then annealed.[15] The as-cleaved GaAs(110) surface displayed a reciprocal-space mirror reflection symmetry $(\bar{h}k)=(hk)$ which was retained in the (1×1) diffraction beams measured at all overlayer coverages studied. The symmetry is the result of the mirror plane symmetry of the real-space-surface unit cell. This symmetry appeared also to be satisfied by the fainter sixth-order spots.

Not only the diffraction spot profiles, but also the diffraction spot intensities were used to characterize the changes induced by the growth of an overlayer. In Fig. 4 the I-V curves for the $(1\bar{2})$ diffraction spot are plotted. The results for a range of bismuth coverages from 0 to 2 monolayers are presented. The films for this set of measurements were prepared and measured at room temperature. Each I-V curve was measured after a background intensity generated by incoherent scattering had been subtracted out. This data is representative of the changes incurred by all of the diffraction beams observed from the surface. It was also noted that, judged subjectively, the background intensity of the diffraction spots for the bismuth films was approximately twice that observed for antimony overlayers.

Motivated by the observation in Fig. 4 that there seems to be a continuous change in the I-V curves as the coverage increases, the I-V curves themselves were selected to provide an independent means with which to characterize film growth. The changes in the I-V curves with antimony and bismuth deposition are quantified in Fig. 5. The coverages quoted are those determined by the QCO calibration. Figure 5(a) is the plot of the intensity of the (10) diffraction beam as a function of overlayer coverage. The data is integrated over 50 to 300 eV and normalized to the zero-coverage value. The (10) beam is a strong beam for clean GaAs(110) due to the reconstruction of the surface.[2] If the clean surface were planar, however, the (10) beam would essentially vanish by the destructive interference of the diffraction waves from the surface unit cell due to the similarity of the gallium and arsenic scattering factors. It can be seen from the diagram that the (10) intensity decreases monotonically up to 1 monolayer for each overlayer system. The inference drawn is that the overlayer causes the substrate reconstruction to relax back into the truncated bulk geometry for both the antimony[4] for the bismuth[7] systems. The relaxation seems to be more complete for the bismuth case than for the antimony case.

A more comprehensive estimate of the changes induced by the overlayer deposition can be derived using a reliability factor analysis of an entire set of diffraction spots. This is given in Fig. 5(b). Here the nine lowest diffraction beams are compared against a set of clean surface diffraction intensities using the x-ray r (reliability) factor, which is a quantitative measure of differences between two sets of I-V curves. From this perspective, the antimony and bismuth systems track very closely. Note that beyond 1 monolayer, no additional coherent diffraction occurs for either system. In fact, the I-V curves in Fig. 4 at coverages higher than 1 monolayer seem to reduce in intensity with additional bismuth deposition. The reduction in intensity corresponds to increased incoherent scattering, which removes intensity from the diffraction beams, and is due to increased surface disorder in the top, now second, bismuth overlayer.

DISCUSSION

Surface ordering at submonolayer coverages is intertwined with the formation of bismuth-adatom chains, a conclusion that is based on knowledge of the atomic geometry of the analogous antimony overlayer system[4] and on scanning tunneling microscopy results for bismuth.[16] This chain formation is termed epitaxy for reasons enunciated below. In Fig. 1 one observes that the elastic-diffraction spot profile is a strong function of the incident-electron kinetic energy. This is called the size effect and is an indicator of two-dimensional island formation.[17] A similar behavior was reported for the antimony overlayer system.[18] An analysis of the photoemission Ga 3d and As 3d core-level attenuation with overlayer coverage has been performed.[6] It concluded that the data fitted a layer-by-layer growth model up to 2 monolayers. Thus, Figs. 1 and 5, scanning tunneling microscopy,[16] and the photoemission data[6] provide conclusive evidence that the first layer grows two dimensionally as ordered epitaxial islands.

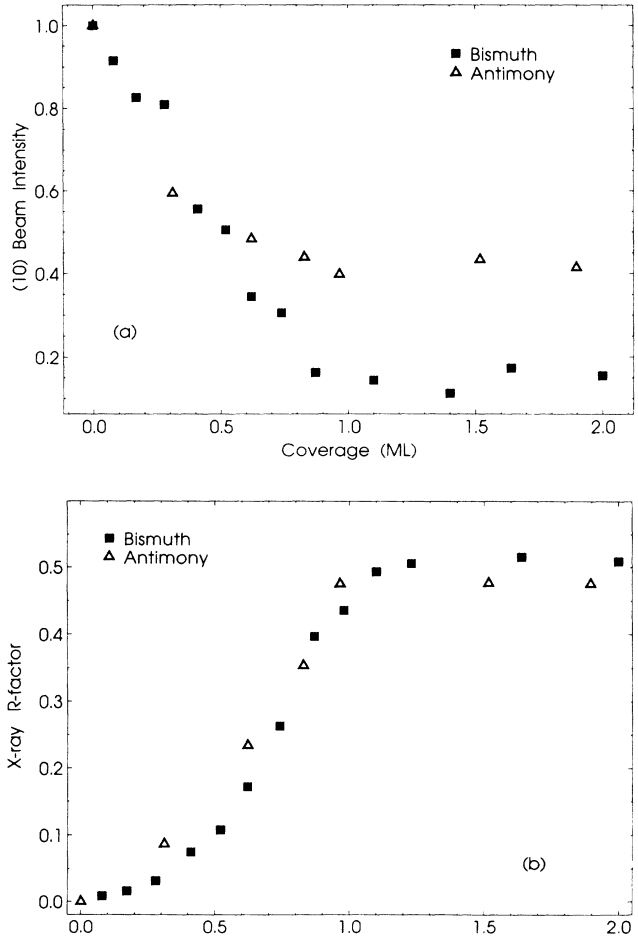

FIG. 5. LEED diffraction beam changes with bismuth and antimony overlayer coverages: (a) normalized (10) diffraction-beam-intensity variation integrated over 50 to 300 eV; (b) x-ray r-factor variation computed for nine diffraction beams.

At coverages beyond 1 monolayer no size effect was observed in the LEED spot profiles and no change in the LEED I-V curves occurred apart from a lowering in absolute intensity. (The x-ray r factor used in Fig. 5 is insensitive to absolute beam intensities, and thus is unchanging at coverages above one monolayer.) This makes the bismuth overlayer growth appear very similar to that of antimony on gallium arsenide. However, the photoemission attenuation analysis draws a distinction between the two systems, with the bismuth overlayer data fitting a layer-by-layer growth model up to coverages of 2 monolayers,[6] whereas the antimony data does not.[13] Hence, the model that evolves for bismuth is one of Stranski-Krastanov growth, where the overlayer forms layer-by-layer for up to 2 monolayers and then suffers increased disorder and three-dimensional islanding at higher coverages. Importantly, the LEED data establishes that the first layer grows epitaxially while the subsequent two-dimensional layer is geometrically disordered.

Figure 2 can be used to infer the nature of island growth at submonolayer coverages. The as-grown film in Fig. 2(a) has considerable disorder in each dimension since the spot width, representing the reciprocal space spread in the diffraction-beam wave vector, is essentially isotropic. Annealing is seen to decrease the spot size, suggesting an increased range of two-dimensional order in the film. However, the annealed spot has an elliptical profile with a 30% spot width reduction along the minor axis and a 24% reduction along the major axis. The minor axis is parallel to the [001] crystal direction, the long axis of the rectangular (110) real-space unit cell. Chains extend perpendicular to this direction.[16] Thus, the observed spot size reduction indicates that there is somewhat more order on the surface in the [001] direction than along the perpendicular [$1\bar{1}0$] chain axis. At submonolayer coverages, islands form with a greater preference for aligning chains parallel to each other than for forming longer chains at the expense of shorter ones.

The preference for bismuth chain ordering perpendicular to the [$1\bar{1}0$] direction can be explained by examining the overlayer-induced lattice strain. For the purposes of discussion we assume that the bismuth overlayer geometry is analogous to that previously determined for antimony overlayers.[4,19] At submonolayer coverages islands might form either by lengthening the chains, up to 24 Å as discussed below, or by stacking chains side by side. The joining of two separated short bismuth chains positioned over the same [110] substrate trough on the

(110) surface would be stabilized by the net amount of energy obtained in bonding the two ends of the chains and would be an energetically favored process at very low coverages, for which few long chains have appeared. However, joining chains in this fashion would not significantly reduce the total elastic strain energy induced in the substrate lateral to the two chains. This strain arises mainly because the substrate atomic geometry in the region of an overlayer chain is required to match a neighboring region of clean surface reconstruction. The matching occurs via modification of the second gallium-arsenide layer geometry since there are no direct bonds between parallel gallium-arsenide chains in the top most substrate layer. Geometric reconstruction is an important property of the (110) surface and probably extends three layers into the bulk.[20]

Alternately one might consider two parallel chains lying in different troughs, separated by a region of normally reconstructed clean surface. Joining two chains laterally in this fashion would not form a direct chemical bond but would reduce the total strain energy because the number of edges is reduced from four to two. In the reconstruction process, the top layer gallium-arsenide atomic geometry between the bismuth chains would take on the truncated bulk geometry, as required by the results of Fig. 5(a), removing the strain between the chains. This might be energetically favored at coverages where long chains are prevalent. It is also an energy-lowering reconstruction process that could continue with the inclusion of additional parallel chains to form two-dimensional islands. Thus, an attractive force between chains directed perpendicular to the $[1\bar{1}0]$ chains arises. It can be thought of as being mediated by the bonds in an underlying gallium-arsenide layer. The same description would be applicable to either bismuth or antimony island growth.

The quantitative analysis of the LEED *I-V* data is currently underway in order to obtain the detailed atomic geometry of Bi/GaAs(110) surface.[19] The most probable geometry to expect is the one analogous to the zigzag chain geometry determined previously for Sb/GaAs(110). However, such a chain would be strained if antimony were simply replaced by bismuth because the bismuth atom is larger than antimony. For example, the covalent radius of bismuth is 1.46 Å and that of antimony is 1.40 Å. This difference in atomic size could be expected to lead to bond-angle and bond-length strain energies. One way the strain could be relieved is by the formation of geometric defects within the surface overlayer. Recent scanning tunneling microscopy of the 1-monolayer film indicates that bismuth indeed forms a chain structure that is punctuated occasionally by a missing adatom defect.[16] The typical chain length is approximately 24 Å.

It is difficult to generalize the results of scanning tunneling microscopy to learn about the long-range geometry of a surface because, by its very nature, the scanning tunneling microscope is a short-range probe of the local surface electronic charge density. Being a diffraction tool, the LEED technique represents a more natural choice to use to determine the average geometry on the scale of 100 to 500 Å across a surface.[21] Hence, the LEED data represented in Fig. 3 provides convincing evidence that the 24-Å chain length is characteristic of the long-range surface geometry of the Bi/GaAs(110) system. In Fig. 3 the satellite diffraction spot is sixth-order spot, corresponding precisely to a six unit cell, or 24 Å, periodicity along the $[1\bar{1}0]$ chain direction. Judging from the elliptical shape of the sixth-order spot the distribution of chain lengths on the surface is clearly centered on 24 Å. Nevertheless, because the intensities of the sixth-order spots are generally weaker than those of the integral-order diffraction spots, cf. Fig. 3, the primary periodicity of this surface remains that of the (1×1) unit cell. The periodicity is only weakly perturbed by the larger unit cell which gives rise to the sixth-order diffraction. The satellite diffraction spots are much broader than the integral-order spots in the [001] direction. This indicates increased disorder along the direction perpendicular to the chain, as though the 24-Å chains were laid down in parallel, but without precisely lining up the endpoints. Such a picture is consistent with the results of scanning tunneling microscopy.[16] Finally, annealing films grown at room temperature did not effect any significant change in the diffraction data. Hence, the bismuth chain appears most stable with the 24-Å average length. No evidence of sixth-order diffraction was found for antimony films.

Sixth-order diffraction was most pronounced at monolayer coverages. If chain elongation were to dominate the epitaxial growth, then upon annealing longer chains would have formed at the expense of the shorter ones until a length of 24 Å was obtained. There is no evidence of this. Thus, a perpendicular interchain force, suggested above, must dominate the ordering until a coverage near saturation at 1 monolayer is reached.

The Bi/GaAs(110) system is an example of how long-range epitaxial forces can impact the nature of overlayer formation on covalent semiconductor surfaces. The geometry of the overlayer is clearly dictated by the underlying substrate geometry. There is a distinct relationship, albeit not simple, relating the substrate periodicity to the overlayer and giving rise to the (6×1) unit cell. The long-range order that gives rise to the sixth-order diffraction beams is most simply explained as a result of the commensurate alignment of the chemically preferred overlayer chain geometry and the underlying lattice periodicity. However, from a comparison of the diffraction spot intensities of the integral- and sixth-order beams, it is clear that to a very good approximation the overlayer is a (1×1) structure. In turn, the geometry of the substrate is modified in a regular fashion by the presence of the overlayer, evidenced by the extinction of the (10) beam. The formation of ordered islands seems to be governed primarily by a strain force that extends between chains through the underlying substrate. This produces elliptical spot profiles at submonolayer coverages. Finally, there is evidence that the consequences of an epitaxial geometry influences the electronic structure. Bismuth is a semimetal and not normally covalently bonded. For example, bismuth forms no III-V compounds as does antimony. However, preliminary indications of the dynamical LEED structure analysis in progress[19] and valencephotoemission studies[16] are that the gallium-arsenide substrate template serves to impose a high degree of directional bonding in the bismuth overlayer, although whether it is best described as p^3 or sp^3 is uncertain at present. This, in turn, should have serious consequences on the energy levels and electron-orbital character of surface states for this system.

ACKNOWLEDGMENTS

The authors would like to acknowledge and thank Mingde Xu and Richard J. Smith for performing the Rutherford backscattering measurements. This work was supported by a grant from the National Science Foundation Grant No. DMR-87-05879.

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