Electronic and structural properties of a discommensurate monolayer system: GaAs(110)-(1×1)Bi

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(Received 24 October 1988)

We report the structural and electronic properties of a new ordered Bi(1×1) overlayer on cleaved GaAs(110) surfaces. Although some structural similarities exist between the ordered Bi monolayer and that for Sb, our studies show the following novel features: a periodic one-dimensional array of misfit dislocations, which appear to generate acceptor states that "pin" the Fermi level on *n*-type GaAs, and Bi-derived valence and conduction bands that extend into the GaAs band gap and are separated by 0.7 eV.

Although several ordered monolayer (ML) and submonolayer systems have been discovered on clean Si and Ge surfaces,[1-4] relatively few have been discovered on the (110) face of compound semiconductors. The most extensively studied epitaxial monolayer system is GaAs(110)-(1×1)Sb.[5-14] This system has served as a useful prototype for experimental[5-12] and first-principles theoretical studies[13,14] alike. Here we present the results of an extensive experimental study of a second ordered monolayer system, namely GaAs(110)-(1×1)Bi. We have studied this system using angle-integrated and angle-resolved photoelectron spectroscopy, scanning tunneling microscopy (STM), and low-energy electron diffraction (LEED). Our results indicate that Bi forms an ordered (1×1) ML on the cleaved GaAs(110) surface with a local structure akin to that of Sb. However, the STM results indicate that, in contrast to Sb, there are misfit dislocations present in the Bi overlayer.

We prepared ordered GaAs(110)-Bi(1 ML) overlayers on cleaved GaAs(110) surfaces (*n*- and *p*-type samples doped to 10^{18} cm^{-3}) by exposing freshly cleaved surfaces to a molecular beam of Bi at room temperature. In this paper we restrict our discussion largely to the ordered monolayer system [1 ML≡GaAs(110) surface density=8.85×10^{14} cm^{-2} ≈3 Å Bi]. LEED patterns taken from the GaAs(110)-Bi(1 ML) system indicated a (1×1) overlayer symmetry. Further support for an epitaxial overlayer structure was obtained from (1) the rapid attenuation of substrate core-level signals with Bi coverage, (2) the observation of a symmetric doublet (split by 0.38 eV) in the Bi 5*d* core level—as for Sb, indicating separate bonding to As and Ga atoms[7,10]—(3) a periodicity corresponding to the surface Brillouin zone of the Bi-related features in angle-resolved valence-band spectra, and (4) STM images.

The STM images for ordered Bi overlayers are shown in Fig. 1. Figures 1(a) and 1(b) were obtained from a GaAs(110) surface covered with 0.5 ML of Bi. In Fig. 1(a), the image is displayed in the conventional manner with a grey scale corresponding to surface height. An ordered Bi terrace is seen as the light portions of the image, while the bare GaAs substrate shows up as the darker portions. The Bi terraces appear to nucleate randomly on the surface, and grow laterally in size as the coverage increases. The height of the Bi terrace above the substrate is about 2.6 Å, depending slightly on the tip-sample voltage. Figure 1(b) shows an expanded view of the surface, with the grey scale now given by a directional derivative corresponding to illumination of the surface by a light source positioned in the upper right-hand corner of the image. This shading is chosen to emphasize the small atomic corrugations on the surface. The upper

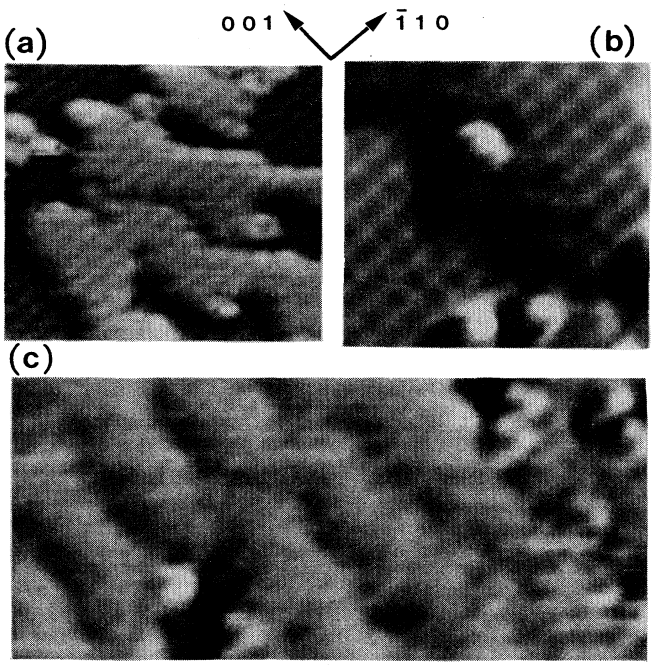

FIG. 1. The structure of ordered Bi overlayers on GaAs(110). (a) 85×80 Å^2 STM image of ordered Bi terraces on GaAs(110). The Bi coverage in both (a) and (b) is 0.5 ML. (b) 55×55 Å^2 view of a Bi terrace (top right) and the GaAs(110) substrate (bottom left). (c) 170×80 Å^2 STM image of a 0.8-ML Bi overlayer showing the misfit dislocations (dark lines running from top left to bottom right).

right half of the image consists of a Bi terrace, and the lower left half is the GaAs substrate. The (1×1) periodic corrugation is clearly evident in both regions (small distortions away from the ideal rectangular unit cell are due to drift in the microscope). It is likely that Bi overlayers have the same geometry as Sb on GaAs(110), which consist of zigzag chains of the group-V element bridging the underlying As–Ga chains. The observed (1×1) overlayer periodicity, two Bi atoms per unit cell, and overlayer height of 2.6 Å, are all consistent with this model. Nevertheless, a complete structural determination by STM requires exceptionally high-resolution voltage-dependent images and careful measurements of the registration of the overlayer corrugation relative to that of the substrate, as has been presented elsewhere for the Sb overlayers.[12] Such detailed measurements have not been performed for the Bi/GaAs(110) system.

As the Bi coverage approaches 1 ML a novel phenomenon is observed [Fig. 1(c); Bi coverage 0.8 ML]. Both the lateral scale and the grey-scale shading of Fig. 1(c) is the same as Fig. 1(a), although the atomic corrugation in Fig. 1(c) is small, possibly due to a blunt probe tip. We see a periodic series of dark lines in the image, extending the [001] direction. The average separation between the lines is about 25 Å, corresponding to six unit cell lengths in the $[1\bar{1}0]$ direction. These dark lines represent a region of the surface which is depressed, due to the absence of Bi adatoms. Thus, the dark lines are dislocations, where one or more Bi atoms are missing. The dislocations form a periodic series of parallel lines on the surface. Looking back to Fig. 1(a), we see there what appears to be a single dislocation extending through the middle of the Bi terrace. We associate these dislocations with a misfit in lateral size between the Bi overlayer and the underlying GaAs substrate. The misfit dislocations probably relieve strain in the overlayer. Both the presence of the dislocations, which on average are separated by 12 Bi—Bi bonds, and their absence for Sb/GaAs(110), are consistent with the $\sim9\%$ larger metallic radius of Bi compared to Sb.

The shapes and size distributions of Bi clusters at 0.5-ML coverages suggests that the in-chain strain plays an important role in the growth kinetics of the layer. The Bi nucleates randomly and grows nonpreferentially until the chain lengths reach the strain-limited critical length. Further two-dimensional growth then occurs only in the [001] direction, which results in the elongated islands shown in Fig. 1(a). As clusters near critical size meet they do not coalesce, but rather maintain their common boundary in the form of the dislocation consisting of missing Bi atoms. Some atomic rearrangement appears to occur as the layer approaches full coverage, as the dislocation network becomes more uniform [Fig. 1(c)].

We have studied the occupied electronic structure of the GaAs(110)-(1×1)Bi(1 ML) system using photoelectron spectroscopy. An estimate of the extent to which the Bi overlayer modifies the electronic structure of the clean surface can be made by taking the difference of two angle-integrated spectra. This is done by subtracting a background spectrum from that of the GaAs(110)-Bi(1×1) system. An appropriate background could be a spectrum of the clean surface,[10] or simply one taken at a different photon energy $h\nu$. In the latter case, the spectral features of the overlayer can be suppressed because of decreases in the photoionization cross section. Here, for brevity, we show in Fig. 2 [curve (a)] only the difference between two spectra of the GaAs(110)-Bi(1 ML) system for $h\nu=90$ and 140 eV, respectively. In this energy range the cross section of the atomic Bi $6p$ level decreases three- to fourfold.[15] A similar attenuation was observed for the Bi overlayer, particularly for the strong feature labeled $S_{5,6}$,[16] which indicates an almost pure p_z-orbital character of this feature. Consequently, $S_{5,6}$ is considerably enhanced in the difference spectrum. This peak, as well as the other features, marked $S_{1,2}$ and $S_{3,4}$, have been labeled according to the principal Sb-induced valence bands of the Sb/GaAs(110) system,[13,14] to which the present system has a spectral resemblance.[10] A lesser feature is observed 6 eV below the valence-band maximum (VBM), which will be discussed elsewhere.[16]

Having established the Bi-related features, we can now study these in more detail with angle-resolved photoemis-

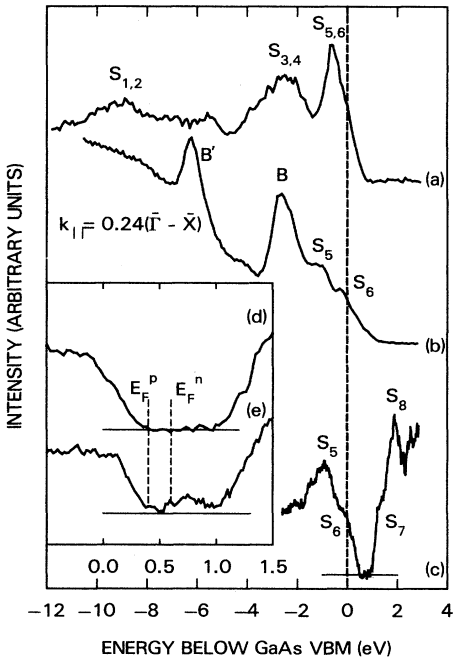

FIG. 2. The electronic structure of a (1×1) Bi monolayer on p-type GaAs(110): (a) Difference spectrum of angle-integrated photoemission spectra taken with $h\nu=90$ and 140 eV. (b) An angle-resolved photoemission spectrum collected from the GaAs(110)-Bi system using an incident photon energy of 22 eV (see the text). STM spectrum on an ordered Bi terrace showing both occupied (S_5 and S_6) and unoccupied (S_7 and S_8) Bi-induced features; this spectrum exhibits a zero-current gap of 0.6 eV. The inset shows expanded STM spectra of the Bi gap region: (d) corresponds to a terrace region different from curve (c); and (e) to an area in the vicinity of a dislocation. The horizontal lines mark the level for zero tunneling current.

sion and STM spectroscopies. Curve (b) of Fig. 2 is an angle-resolved photoelectron spectrum taken from the GaAs(110)-Bi(1 ML) system along the $\bar{\Gamma}-\bar{X}$ direction of the surface Brillouin zone. The spectrum was collected at $h\nu=22$ eV with mixed polarization and with an emission angle of 5° relative to the surface normal. The two features marked B and B' in curve (b) arise from bulk transitions; they have also been seen on both the clean GaAs(110) surface and on the Sb-GaAs(110) system.[8] The other features in the spectra have been marked in accordance with the features in curve (a). Features S_5 and S_6 are assigned to surface resonances, whose origins are probably associated with the Bi-substrate bonds (see later). The initial-state energy of the states did not exhibit any detectable dependence on the perpendicular component of the electron wave vector. Away from the zone center S_6 sharpens up and disperses downwards by ~ 0.5 eV towards the zone boundary ($\bar{X}$). We show the dispersion of both S_5 and S_6 with $k_{\parallel}$ in the $\bar{\Gamma}-\bar{X}$ direction of the surface Brillouin zone in Fig. 3. From these data we conclude that S_6 is a true surface state as it appears above the projected bulk band structure. Furthermore, at the zone center, this band is ~ 0.3 eV above the VBM of GaAs. This location is consistent with the extra emission above the VBM observed in curve (a), and with the results of STM spectroscopy.

A STM spectrum is shown in curve (c) of Fig. 2, acquired and normalized in the manner previously described.[11,12] Its intensity provides a qualitative measure of the surface density of states. The spectrum was obtained from an ordered portion of the Bi overlayer. The spectrum displays filled and empty bands of states, separated by a band-gap region in which the tunnel current is zero. A gap width of 0.7 eV is observed in the spectra. On the filled-state side the spectra display two states, labeled S_5 and S_6 , and on the empty-state side two states are also seen, labeled S_7 and S_8. Relative to the GaAs VBM, we find average energies of -0.9, 0.1, 1.3, and 1.9 eV for the peaks S_5-S_8, respectively. For the p-doped type GaAs surfaces, the Bi ML "pins" the Fermi level E_F at the top of the filled Bi states (~ 0.4 eV above the GaAs VBM), as indicated in the inset of Fig. 2. On portions of the surface near the observed misfit dislocations we observe a weak density of empty states within the band-gap region; curve (e) in the inset of Fig. 2 shows these states on an expanded energy scale. For Bi monolayers on n-type GaAs, the Fermi level E_F^n is located near the low-energy edge of the dislocation-induced states, which suggests that these acceptorlike states appear to be responsible for the pinning. Defect-induced states are observed as well at submonolayer coverages near the edge of Bi terraces;[16] they appear to emerge from the Bi conduction-band states and are thus similar to those observed for Sb on GaAs.[11] Their origin is associated with the edge atoms. A similar relationship may be assumed for the defect states at the dislocations, as these consist of adjacent terraces separated by a row of missing atoms. This notion is supported by the smooth changes of the Fermi level with coverage,[16] which indicates an evolutionary development of defect levels high in the band gap at low coverage to a position near midgap at full coverage, in agreement with the STM spectroscopic results. Beyond monolayer coverages, the Fermi levels remain "pinned" at their separated positions indicated in the inset of Fig. 2, which implies that neither metal-induced gap states[17] nor screening effects[18] can be attributed to the semimetallic Bi.

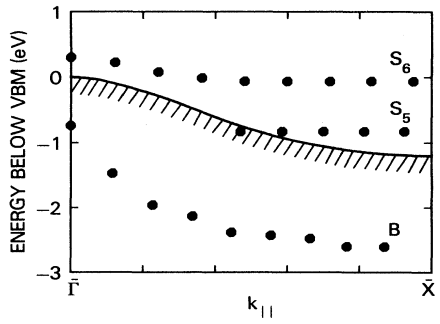

FIG. 3. The initial-state dispersion of S_5, S_6, and B, along $\bar{\Gamma}-\bar{X}$, determined using angle-resolved photoemission; the shaded region is the projected bulk GaAs band structure.

We will briefly discuss the origin of the observed spectral features in terms of the two different bonding models proposed for Sb/GaAs(110). For this system, the zigzag chains of Sb run parallel and in between the underlying As–Ga chains along the $[1\bar{1}0]$ surface direction. Thus the Sb atoms are triply bonded by two planar bonds to adjacent Sb atoms and a backbond, which alternates along the chain, to either a Ga or As atom in the lower plane. The simplified orbital pictures proposed for the Sb layer consist of an sp^3 (tetrahedral) (Ref. 13) or a p^3 (pyramidal) (Ref. 14) bonding scheme, each with two surface bonds to adjacent Sb atoms and a backbond to a substrate atom (either Ga or As). The major difference lies in the proposed existence of a filled, dangling-bond-like state protruding from the surface for the sp^3-bonded model, to which the states $S_{5,6}$ may be attributed.[8,13] Mailhiot *et al.*,[14] on the other hand, assign these states and the empty $S_{7,8}$ states, respectively, to bonding and antibonding levels of the Bi-substrate backbonds. Thus far, experimental results cannot make a clear-cut distinction between these two bonding configurations for Sb. However, Bi, unlike Sb, is not known to form tetrahedrally coordinated compounds, which would suggest the probable absence of a filled dangling-bond-like sp^3 state. Support for this notion is provided by the p_z character of the $S_{5,6}$ feature in Fig. 2(a), discussed above. Nevertheless, further theoretical and experimental studies are required to resolve this issue.

In summary, we have presented a multitechnique approach in characterizing the structural and electronic properties of a novel discommensurate adlayer system. This system, due to the larger atomic size of the Bi, forms a one-dimensional array of dislocations in the overlayer, which generate acceptorlike states. Between dislocations, the one-to-one correspondence between substrate and overlayer atoms results in a nearly ideal system, characterized by a two-dimensional semiconductor band struc-

ture with a band gap of ~ 0.7 eV lying wholly within the band gap of the GaAs substrate.

The valuable technical assistance of A. Fein, A. Marx, and M. Prikas is gratefully acknowledged. Part of this research was done at the National Synchrotron Light Source (NSLS II), Brookhaven National Laboratory (Upton, NY), which is funded by the U.S. Department of Energy.

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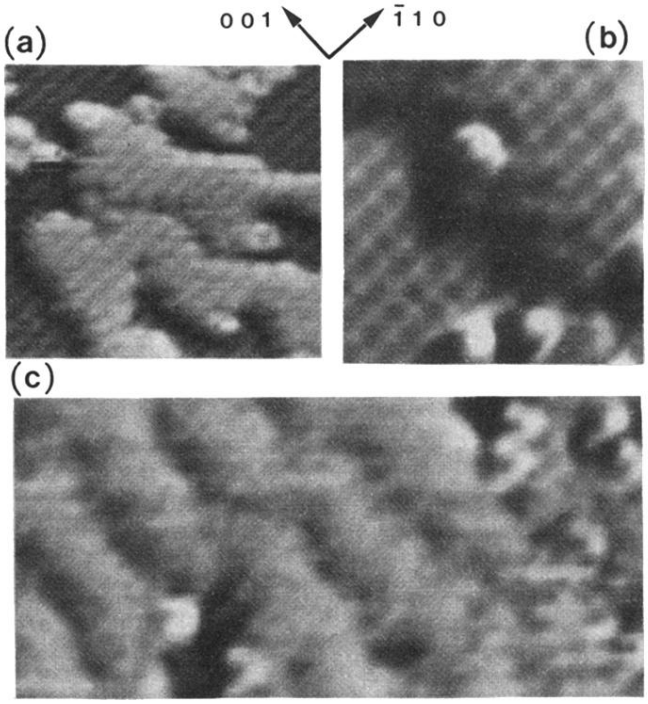

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