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Ab initio investigation of Bi-covered GaSb(110) surfaces

S. C. A. Gay and G. P. Srivastava
School of Physics, University of Exeter, Stocker Road, Exeter EX4 4QL, United Kingdom

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We present theoretical studies for the Bi chemisorbed GaSb(110) surface using *ab initio* pseudoptential calculations. Our results give strong support that the metastable (1×1) phase is best described by the epitaxially continued layer structure. We also investigate a number of structures for the stable (1×2) phase and conclude that the system is best described by the modified epitaxially continued layer structure mechanism reported by van Gemmeren *et al.* The calculated electronic structure is found to be in excellent agreement for both phases with angle-resolved ultraviolet photoemission spectroscopy data presented by McIlroy *et al.*, whereas geometric parameters agree excellently with those obtained by van Gemmeren *et al.*

I. INTRODUCTION

Single-monolayer (ML) coverage of III-V semiconducting surfaces by group-V materials has received considerable attention over the last decade[1] both experimentally and theoretically. In the case of 1-ML Sb coverage on the (110) surface of GaP,[2] GaAs,[3] InP,[4] and InAs,[5] a clear (1×1) surface symmetry is observed by low-energy electron diffraction (LEED). In contrast Bi appears to behave somewhat more unpredictably. Full single-monolayer coverage of Bi on GaAs(110) surfaces is difficult to achieve. Due to the substrate lattice parameter (5.65 Å) being too small to accommodate the Bi atom chains, missing adatoms are observed, one in every six (1×1) unit cells along the Bi chains.[3,6,7] On the other hand, substrates with larger lattice parameters, such as InP (5.87 Å),[4] InAs (6.06 Å),[8,9] and GaSb (6.10 Å),[10–13] are better able to sustain a full monolayer coverage of Bi.

The general consensus for 1-ML Bi deposition on III-V(110) surfaces is a (1×1) phase[10,14] with the epitaxially continued layer structure (ECLS) proposed by Skeath *et al.*[15] In this model, two Bi adsorbate atoms occupy the sites that would have been occupied by the next III-V basis pair. Simple electron counting considerations show that this arrangement produces fully occupied bonds between the adatoms and the substrate and between the two adatoms in each unit cell. The two adatoms having identical electronegativity means that only small charge transfer between them can take place resulting in an adatom chain that has a small tilt with respect to the surface. This is in contrast to clean III-V(110) surfaces where the atomic chain in the top layer is tilted considerably due to different electronegativities of the anion and cation leading to an asymmetry in the charge distribution across the chain. The tilt and the considerable substrate distortion associated with it are almost entirely removed by deposition of a group-V adlayer, with the top layer substrate atoms returning close to their bulk positions.

In the case of 1-ML deposition of Bi on a GaSb(110) substrate, van Gemmeren and Johnson[14] confirmed, using photoelectron spectroscopy, low energy electron diffraction and more recently using x-ray diffraction,[13] that for the (1×1) phase the ECLS is the correct geometrical model. However, this phase is only metastable, and indeed after anealling a stable (1×2) reconstruction is observed.[14,16] A similar observation is made for Bi deposition on InAs(110) with its lattice parameter close to that for GaSb.[16,9] Likewise, Bi deposition on an InSb(110) substrate, which has a lattice parameter larger than GaSb at 6.48 Å, results in (1×2) and (1×3) phases.[16]

Various explanations have been put forward for the process behind the $(1\times1)\rightarrow(1\times2)$ transition of a Bi ML on a GaSb(110) surface, and proposals made for the final structure of the surface. From their photoemission experiments, McIlroy *et al.*[11] support a picture where the (1×2) reconstruction is composed of a combination of the ECLS model and the epitaxially on top structure (EOTS). They are also not entirely convinced from their results that the (1×1) phase of Bi/GaSb(110) [or Bi/InAs(110) (Ref. 8)] is due to the ECLS, but only that the structure is based on the formation of Bi chains along the $[\bar{1}10]$ direction. In a recent paper, van Gemmeren *et al.*[10] report a mechanism for the (1×2) reconstruction consisting of two Bi chains similar to those of the ECLS, but this time with a top layer Ga-Sb basis pair missing. For this model to work, significant charge transfer has to take place from one Bi chain to the other. This model is somewhat more complicated than that put forward by McIlroy *et al.* However, a point that is not stressed in the paper by McIlroy *et al.*[11] is that the concept of a mixed EOT and ECL structure corresponds to at least four distinctly different structures. These four structures are shown in Fig. 1. The main reasoning behind this model was that McIlroy *et al.* concluded that the Bi chains remained intact during the $(1\times1)\rightarrow(1\times2)$ phase transition. However, the model proposed by van Gemmeren *et al.* does not violate this principle. More detailed accounts of the geometrical results obtained by van Gemmeren *et al.* have been published in another work by Lottermoser *et al.*[17]

One point in the literature that would appear crucial in determining which of these models might apply to the (1×2) structure is the ratio of Bi-Sb to Bi-Ga backbonds. In the model proposed by van Gemmeren *et al.* these two types of backbonds are present in equal ratio, whereas in the model proposed by McIlroy *et al.* these backbonds are in ratio of 2:1 or 1:2. For example in Figs. 1(a) and 1(c) there are twice as many Bi-Ga backbonds as Bi-Sb whereas in Figs. 1(b) and 1(d) it is the other way around. Though Gavioli *et al.*[18] found that there were more Sb-Bi than Ga-Bi bonds, van Gemme-

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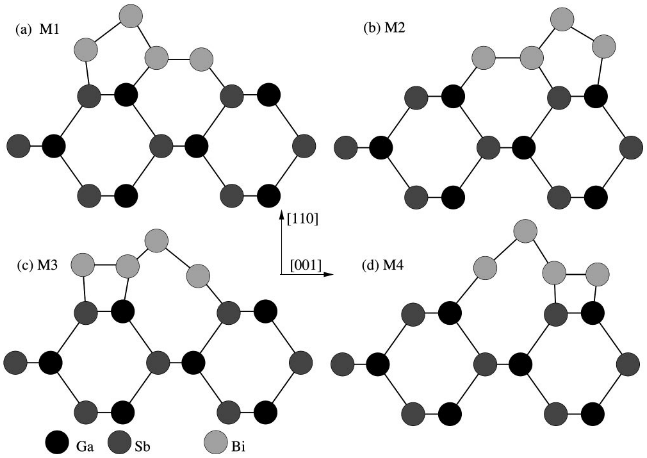

FIG. 1. Diagram showing the four different models consistent with the idea put forward by McIlroy *et al.* (a) has the EOTS chain to the other side of the ECLS chain than in (b), which is the version shown by McIlroy, whereas the chains in (c) [and (d)] have the same relative orientations as in (a) [and (b)] but with the reverse vertical relative orientation.

ren *et al.*[10] later found that these bonds were in fact present in equal proportions. This was concluded from almost equal intensities for shifts in the core-level spectra for the components Ga $3d$ and Sb $5d$. It should be noted that for the (1×1) system these shifts were not observed, since the substrate atoms were close to their bulk configurations. This indicates that substantial reconstruction of the substrate atoms must be occurring in the (1×2) case. This was seen to be at variance with the assumed almost bulklike substrate in the model proposed by McIlroy *et al.*

The present study sets out to do two things. First, we will compare the (1×1) EOTS and ECLS models and predict which of the two we believe that the GaSb(110)(1×1)/Bi(1 ML) system will take up. Second, we will address the (1×2) reconstruction. This part will itself be divided into two stages. Initially, just the four McIlroy models will be compared to one another in order to determine which is the most favorable of these. This structure will then be compared to the stoichiometrically inequivalent structure proposed by van Gemmeren *et al.* These two structures can also be compared to the (1×1) metastable phase [augmented to a (1×2) unit cell for the sake of compatibility]. This should enable us to predict a theoretical structure for the (1×2) reconstruction and enable us to discuss it in the context of existing experimental data.

II. METHOD

The results of all calculations presented in this paper are obtained by using the density-functional theory in its local approximation. The Ceperley-Alder electron correlation scheme is used in the form parametrized by Perdew and Zunger.[19] Ion-electron interactions are treated by using the norm-conserving pseudopotentials of Bachelet, Hamann, and Schlüter.[20] Relaxation of atomic and electronic degrees of freedom is achieved by solving the Kohn-Sham equations. Wave functions are expanded using a plane-wave basis set.

We model the surface system in a periodic slab geometry. Our unit cells have the (1×1) or (1×2) periodicity of the zinc blende (110) surface as well as an artificial periodicity introduced in the surface normal direction. The unit cells have a length equivalent to 14 atomic layers of bulk GaSb in the [110] direction. The slabs contain nine layers of GaSb of which the middle three are kept frozen. In all cases Bi coverage is considered on both sides of the slab. This introduction of reflection symmetry allows us to split the Hamiltonian into two matrices each nearly half the size of the original matrix. All nonfrozen atoms are allowed to relax into their minimum energy configuration by using a conjugate gradient technique.[21] Surface geometries were obtained using a 8-Ry cutoff for the plane-wave basis. This cutoff was found adequate, as test results for the (1×1) ECLS model with a 10-Ry cutoff showed only small (within 1%) changes in key structural parameters. Four special **k** points were used for sampling the irreducible segment of the Brillouin zone for both the (1×1) system and the (1×2) system.

III. RESULTS

A. GaSb(110)(1×1)/Bi(1 ML)

1. Energetic and electronic comparison of ECLS and EOTS

Calculations were carried out at the theoretical lattice constant of 6.00 Å for GaSb. Results for both the ECLS and EOTS models for the GaSb(110)(1×1)/Bi(1ML) revealed that the ECLS has a lower energy than the stoichiometrically equivalent EOTS structure. The difference in energy was found to be 0.43 eV per (1×1) surface unit cell in favor of the ECLS. This supports the view held by van Gemmeren and co-workers[13,14] that the GaSb(110)(1×1)/Bi surface is described by the ECLS in the same way that Bi (and Sb) bond to other III-V(110) surfaces.[1]

Our electronic band-structure calculations reveal that the EOTS system is close on the boundary between semiconducting and semimetallic whereas the ECLS is clearly semiconducting. We can make such a distinction with confidence, despite the application of the local density approximation, the use of a lattice constant slightly smaller than found experimentally and our choice of kinetic-energy cutoff. With the two types of surfaces available, the preferred option is usually semiconducting. Furthermore, despite the findings of van Gemmeren *et al.* that the GaSb(110)(1×1)/Bi surface is metallic, McIlroy *et al.* do find it to be semiconducting and report surface states in good agreement with those that we obtain for the ECLS model. Figure 2 shows our band structure results along with the angle-resolved ultraviolet photoemission spectroscopy results (ARUPS) obtained by McIlroy *et al.* The projected band structure shown in their paper has a larger stomach gap than ours, but as can be seen in Fig. 2, the calculated state which in our diagram lies close to the top edge of the large stomach gap shows very similar dispersion to that reported by McIlroy *et al.* (shown as squares). The agreement between the experimentally obtained ARUPS data and the occupied surface states from our calculations is very good indeed. Agreement between the ARUPS data and our calculated EOTS bands (not presented here) was also found to be quite good. Based upon the ARUPS measurements McIlroy *et al.* could not confidently distinguish between the ECLS and EOTS models as was indeed the case with our own calculations. However, we would argue that this agree-

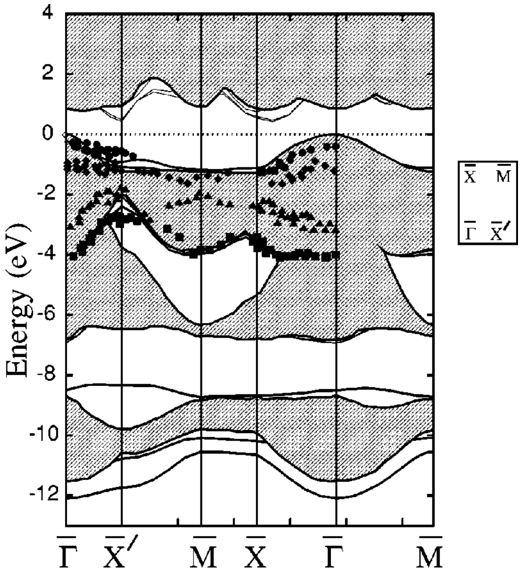

FIG. 2. Band structure for the GaSb(110)(1×1)/Bi(1 ML) system with ECLS termination. The hatched region corresponds to the bulk projected band structure for GaSb(110). Occupied surface states are shown as thick black lines, whereas unoccupied surface states are shown as thin black lines. The plot additionally shows the ARUPS data reported by McIlroy *et al.* shown as squares, triangles, lozenges, and circles.

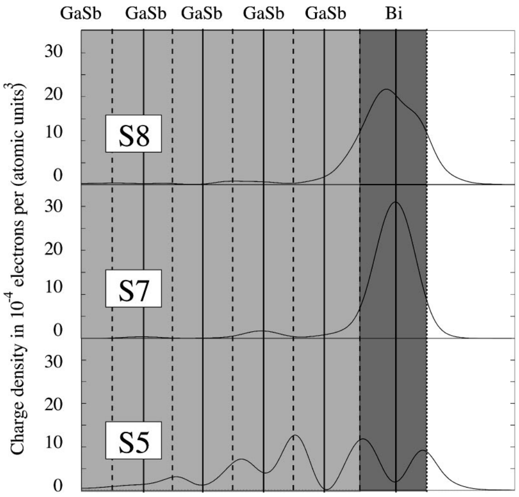

FIG. 3. Planar averaged partial charge densities at $\overline{X'}$. S_8 and S_7 correspond to the highest and second-highest occupied surface states, respectively and S_5 to the stomach gap state.

ment between the ARUPS and calculated EOTS states is not as good as in the case of the ECLS bands, particularly in the band gap region where the dispersion of our EOTS surface bands is somewhat different, with positive dispersion of the highest occupied state along the second half of the $\bar{\Gamma}$ to $\overline{X'}$ segment.

The dispersion of all the states shown in Fig. 2 is consistent with the generic picture established for Bi overlayers on other III–V(110) substrates within the (1×1) ECLS surface reconstruction.[1,21] In our discussion we will follow the nomenclature used in Ref. 21 as far as possible.

The two states below the bulk valence band (S_1 and S_2 in Ref. 21) are strongly localized and are due to the *s* orbitals of the Bi atoms and the underlying substrate atoms. The split in energy arises from the two different chemical environments experienced by the two Bi atoms—one is bonded to a Ga atom, the other to an Sb atom. For Bi on GaAs(110) and InAs(110) substrates, the higher of these two states was found just in the ionic gap, whereas for InP(110) it was found to be resonant with the *s*-like bulk states.[21] There are of course many factors contributing to the positions of these bands. In all cases the lower of the *s*-type bands is localized on the Bi atom bonded to top-layer substrate anion whereas the higher of the two is localized on the Bi bonded to cation.

The electronegativities of Ga, In, P, As, Sb, and Bi, presented in Table I, are a very useful parameter in determining and understanding the trends outlined above. Considering the immediate environment of the Bi-Bi chain we see that to one side it is bonded to a cation (Ga in this case), which has a lower electronegativity than Bi, and to the other it is bonded to an anion (Sb in this case), which has a larger electronegativity than Bi. It should be noted that the difference in electronegativities of the substrate cations and anions in Ref. 21 were much larger than is the case for GaSb. It is therefore not surprising then that the energetic separation between the two *s* bands is much smaller for a GaSb substrate than for the much more polar substrates in Ref. 21. The actual positions of these states relate largely to the energy of the *s* states of the two atoms involved, a view that is easily verified by comparing the band structures for a Bi overlayer on various III-V(110) substrates (cf. Fig. 2 and Ref. 21). As the position of the bulk *s*-like states does change considerably for different III-V substrates, the positions of these surface states may lie either above or below the bulk *s* continuum.

The state observed in the ionicity gap is slightly different in nature for this system than those labeled S_3 in Ref. 21, where it was reported as being a $ss\sigma$ antibonding combination between the top-substrate anion and the Bi atom to which it was bonded. At the $\overline{X'}$ point, though there is some Bi–Sb $ss\sigma$ antibonding character, this state is in fact predominantly $ss\sigma$ antibonding between the two Bi atoms of the ECLS chain.

The ARUPS data presented by McIlroy *et al.*[11] relate to the four highest occupied states corresponding to the states S_5 to S_8 in Ref. 21 and as such it is these states that allow us to make the comparison between experiment and theory. In their paper, McIlroy *et al.* conclude from bandwidth considerations that the two states at the top of the stomach gap are due to an interaction between the top-layer substrate atoms and the Bi chains. Though we find the higher of these two states to be resonant with the bulk, the lower of the two (S_5 in Ref. 21) is localized around the Bi-substrate interface as is shown by the planar averaged charge density plot for this state in Fig. 3. The orbital nature of this state is found to be an interaction between the p_z orbitals of the top-layer Sb atom with the adjoining Bi atom [see Fig. 4(a)]. This is very similar to the analogous state reported for the systems in Ref. 21 and for the InP(110)-Sb system.[22] In contrast to the two

TABLE I. Pauling electronegativities.

Ga	In	P	As	Sb	Bi
1.81	1.78	2.19	2.18	2.05	2.02

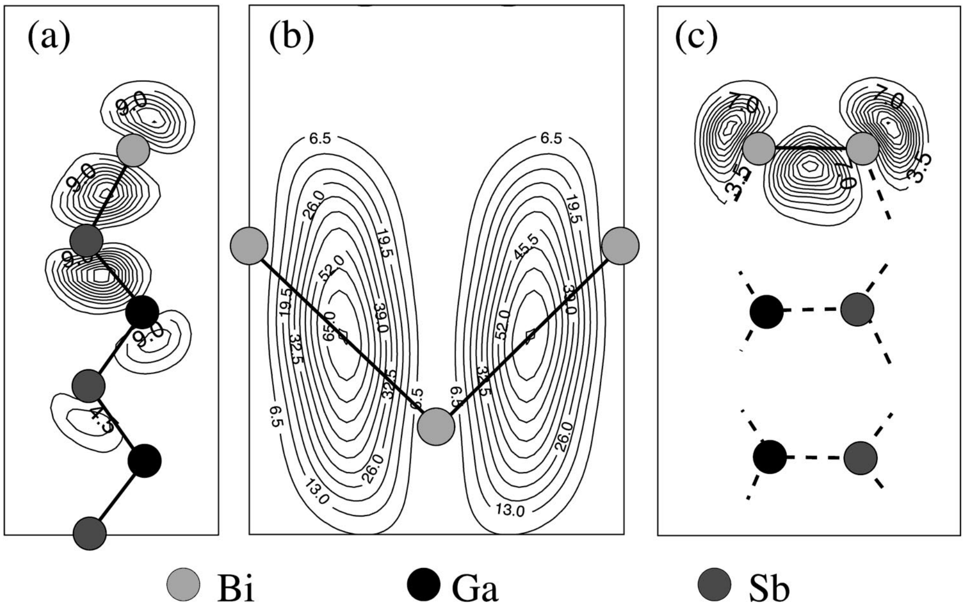

FIG. 4. Planar partial charge density plot at $\overline{X'}$ for (a) vertical slice through chain containing a Ga atom in the top substrate layer for the state in the stomach gap, (b) horizontal slice through the Bi chain for the second-highest occupied surface state, and (c) vertical slice containing Bi chain for the highest occupied state. These correspond, respectively, to S_5, S_7, and S_8 in Fig. 3.

stomach gap states, McIlroy *et al.* concluded that the two highest occupied surface states were entirely localized on the Bi adsorbate layer. This is at variance with the generic picture observed in Ref. 21, where both these states showed some interaction with either the top layer cation or anion. However, in the case of the Bi/GaSb(110) system we must concur with McIlroy *et al.*, finding both of these states to be entirely localized on the top Bi layer. At the $\overline{X'}$ point the second highest occupied surface state is sharply localized on the Bi layer [Fig. 3(b)] and is associated with $pp\sigma$ bonding between Bi atoms [Fig. 4(b)]. This is considerably different from the analogous states reported in Ref. 21 where this state corresponded to an interaction between the top layer anion p_{xy} orbitals and the adjoining Bi p_z orbitals. The highest occupied state is seen to be localized more broadly around the Bi layer height and is found to be due to a π-like bonding arrangement [Fig. 4(c)]. The top two states remain localized on the Bi layer throughout the Brillouin zone, but their orbital character does change. For example, at the $\overline{X}$ point the highest occupied state is associated with the p_z state of the Bi atom bonded to Ga.

2. ECLS and EOTS geometry determination

Tables II and III show our geometrical results for both the ECLS and EOTS corresponding to a theoretical lattice constant of 6.00 Å. The x-ray diffraction measurements[13] shown in Table II are obtained using the fractional coordinates from Ref. 17 and a lattice parameter of 6.096 Å. Agreement between our results and the x-ray diffraction results is very good. Our top-layer Ga-Sb bond length is the same as our theoretical bulk bond length in agreement with van Gemmeren *et al.*[13] who noted from their x-ray data that the top-layer Ga-Sb bond length corresponded to the bulk value. Furthermore, we find that all our Ga-Sb bond lengths differ little from the bulk value in this calculation.

The bond length parameters obtained for the EOTS are very close to ECLS values. The tilt angle of the Bi-Bi chain with respect to the (110) plane in our calculations was obtained using $\omega_{t1}=\tan^{-1}(\Delta_{\perp 1}/\Delta_{y1})$. This leads to a small value of about 1.3° for both the ECLS and EOTS. The value reported by van Gemmeren is about $3°\pm 2°$, which is not far off and also very small. However, there is a significant difference between the ECLS and EOTS for the angles ω_2 and ω_3. For the ECLS they are close to the tetrahedral bond angle, in agreement with Refs. 13 and 17. For the EOTS these are close to 90°.

The tilt of the Bi ECLS chain in this study differs in two ways to that encountered for GaAs, InP, and InAs (110) substrates.[21] The tilt angle of the Bi chain is smaller in magnitude and different in direction for a GaSb substrate than for GaAs, InP, and InAs substrates. In the latter cases the tilt of the Bi chain was found to cluster around 5° with *opposite* inclination to the tilt of the top-layer substrate chain. The tilt of the Bi chain on the GaSb(110) is only 1.3°, with the *same* inclination as the top substrate layer GaSb chain. However, the tilt of the top-layer substrate chain $\omega_{t2}[=\tan^{-1}(\Delta_{\perp 2}/\Delta_{y2})]$ for the present ECLS case is very similar to those reported in Ref. 21 at 5.0° with the cation

TABLE II. Structural length and separation parameters in Å obtained for (1×1) structure as defined by Fig. 5.

	Bi–Bi	Bi–Ga	Bi–Sb	Ga–Sb (top layer)	Δ_{y1}	Δ_{y2}	$\Delta_{\perp 1}$	$\Delta_{\perp 2}$
ECLS (LDA)	2.96	2.63	2.88	2.60	2.07	1.50	0.04	0.13
EOTS (LDA)	3.00	2.71	2.91	2.56	2.13	1.43	0.05	0.16
X-ray diff. (Ref. 13)	3.03	2.68	2.81	2.64	2.13 ± 0.12	1.61 ± 0.18	0.09 ± 0.17	0.0 ± 0.17

TABLE III. Structural angular parameters in degrees obtained for (1×1) structure as defined by Fig. 5.

	ω_1	ω_2	ω_3	ω_{t1}	ω_{t2}
ECLS (LDA)	91.4	107.9	107.9	1.3	5.0
EOTS (LDA)	89.9	84.9	85.0	1.3	6.4
X-ray diff. (Ref. 13)	93±2	107	109	3±2	0.0

TABLE IV. Relative energies per (1×2) surface unit cell obtained for our density-functional theory calculations for the four different structures shown in Fig. 1. The lowest energy structure $M2$ is used as a reference.

$M1$	$M2$	$M3$	$M4$
0.91 eV	0.0 eV	1.43 eV	0.71 eV

vertically higher than the anion. This demonstrates that the substrate relaxation mechanism remains very similar to that for all the other III-V substrates, but that adsorbate layer relaxation changes as a function of the substrate. In all the Bi/III-V(110) cases the Bi atom bonded to the anion will have more charge than the Bi bonded to the cation since the anion is able to ‘‘draw’’ electrons from the top-layer cation through the Bi chain. However, whereas Bi has a much smaller electronegativity than P or As, it has an electronegativity very close to that of Sb. This should result in more extended covalent type bonds between the Bi and Sb than for the Bi-As or Bi-P bonds in Ref. 21. This argument could account for the difference in the magnitudes of the tilt of the Bi chain on different substrates. The tetrahedral radii of the substrate atoms are also likely to affect the tilt of the surface chain. In fact for all the substrates in Ref. 21, the anion radius is smaller than the cation radius. However, with GaSb the ratio is inverted with Ga having a tetrahedral radius of 1.26 Å and Sb a tetrahedral radius of 1.36 Å. So Bi/GaSb(110) differs in two important ways from Bi on GaAs, InP, and InAs (110) substrates: (i) the adatom has an electronegativity close to the anion and (ii) the anion is larger than the cation. It seems plausible that the second difference could account for the change in orientation of the tilt of the Bi chain.

B. GaSb(110)(1×2)/Bi(1 ML)

1. Energetic comparison of the combined ECLS and EOTS models

The four structures shown in Fig. 1, corresponding to four generic but different geometries consistent with the model suggested by McIlroy *et al.* were allowed to fully relax. $M1$ has the EOTS chain bonded above the ECLS chain to one side and bonded to the top layer Sb atom at the other. $M2$ also has the EOTS chain bonded above the ECLS chain to one side, but this time the other side is bonded to Ga (this structure corresponds to that drawn by McIlroy *et al.* in Ref. 11). $M3$ has the ECLS chain bonded above the EOTS chain to one side and bonded to the top-layer Sb to the other. And finally, $M4$ has the ECLS chain bonded above the EOTS chain to one side and bonded to the top-layer Ga to the other. The total energy of these four structures were then compared to one another, and these energies are summarized in Table IV. Clearly model $M2$ is the lowest in energy, by about 0.71 eV per surface unit cell compared to its nearest contender, $M4$. This difference is significant enough to rule out $M1$, $M3$, and $M4$, and therefore it is $M2$ that we will continue to study further, and compare this structure to that proposed by van Gemmeren *et al.*

However, before proceeding with a comparison of $M2$ with the modified ECLS (1×2) structure, it is worth looking at Table IV and Fig. 1 a little more closely. The two structures that offer the lowest energy ($M2$ and $M4$) are those that have more Bi-Ga than Bi-Sb bonds. From simple tight binding considerations Bi-Sb bonding is usually lower in energy than Bi-Ga bonding, so the energy difference upon change in the backbond ratio (i.e., between $M1$ and $M2$ or between $M3$ and $M4$) must be largely dependent on some other energy, perhaps that of the dangling orbital on the exposed top layer substrate atom. Since less charge transfer from the Bi chains is required to saturate the Sb-dangling bonds than the Ga-dangling bonds, it would be energetically favorable to have Sb-dangling bonds rather than Ga-dangling bonds. On this basis $M2$ is preferable to $M1$ and $M4$ is preferable to M3. This is indeed borne out by our calculations. This clearly shows that the backbond-type ratios play a big part in determining the stable geometry. Additionally, the geometric considerations for the vertical ordering of the ECLS and EOTS can produce significant energy differences. From our calculations we find that a change in the backbond ratio, from $M2$ to $M1$, results in an energy penalty of 0.91 eV. On the other hand, a change in the vertical ordering of the ECLS and EOTS chains, from $M2$ to $M4$, raises the energy by 0.71 eV. Changing the structure from $M4$ to $M3$ (i.e., changing the backbond ratio) leads to an energy penalty of the same order as changing from $M2$ to $M1$. Thus energetically speaking $M3$ is the poorest choice of the four structures considered, since it is disfavored by both the presence of the Ga-dangling bonds (rather than the Sb dangling bonds) and the ECLS chain above the EOTS chain.

2. Structural results for the combined ECLS-EOTS and the modified ECLS GaSb(110)(1×2)/Bi surfaces

In Ref. 10, van Gemmeren *et al.* proposed their modified ECLS model accompanied with geometrical data. More detailed geometrical data is given in Ref. 17. They have compelling experimental evidence to support their structure using scanning tunneling microscopy, surface x-ray diffraction, and photoelectron spectroscopy. McIlroy *et al.* do not support their model with any geometrical data, and stress that it is just one of many possible structures compatible with their photoemission results. Our calculations have shown that in general the combined ECLS-EOTS model is stable, and so we are in a position to compare such structures to that proposed by van Gemmeren *et al*. The modified ECLS model may be seen in Fig. 6, with certain parameters indicated upon it.

Table V shows the values of the angular parameters for the $M2$ combined ECLS-EOTS and the modified ECLS models. The calculated values obtained for the modified ECLS are in excellent agreement with those of van Gemmeren *et al.* A point of interest are the tilt angles of the Bi chain

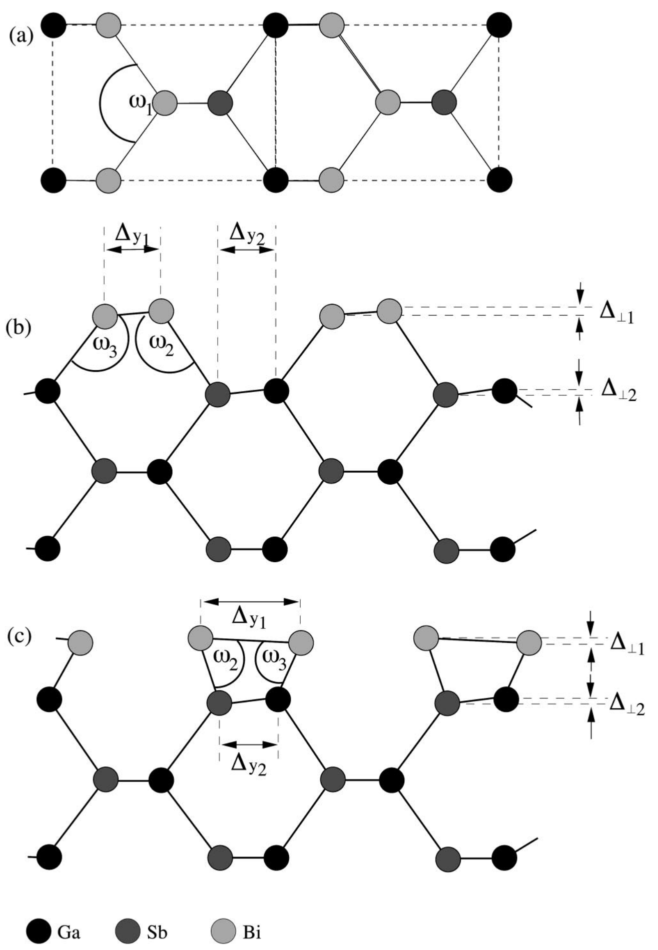

FIG. 5. Schematic diagram showing (a) the top-view and (b) the side view of the ECLS model. (c) shows the side view of the EOTS model. Certain calculated parameters are indicated in the figures.

bonded to Sb and the Bi chain bonded to Ga, respectively, with the (110) plane, labeled ω_{t1} and $\omega_{t3}[=\tan^{-1}(\Delta_{\perp 3}/\Delta_{y3})]$. van Gemmeren *et al.* refer only to the tilt of the Bi chains without distinguishing between the two types of chain present, i.e., one bonded just to Ga atoms and the other only to Sb atoms. The value that they report is $34° \pm 3°$ and is very close to our calculated value ω_{t1} for the Bi chain bonded to Sb atoms only for the modified ECLS. We find that the tilt on the opposite facing chain (ω_{t3}) is a little larger at 38.4° (only just outside their reported error). This chain is only bonded to Ga atoms, and as such experiences different charge transfer through its bonds with the substrate.

Table VI gives certain key vertical and horizontal separation parameters and Table VII gives selected calculated bond lengths. The experimental values given for Bi-Ga, Bi-Sb, and Ga-Sb bonds are those reported in Refs. 10 and 17 whereas the Bi-Bi lengths are obtained from the fractional coordinates in Ref. 17 using a lattice parameter of 6.096 Å. The calculated values for the modified ECLS shown in Table VII provide good agreement with the experimental bond lengths obtained by van Gemmeren *et al*. The biggest discrepancy relates to the lengths of the two Bi-Ga bonds. We obtain considerably smaller difference between the two lengths, but also find that even the longer of the two lengths falls short of the error margins on their shortest length. We also remain unclear about the location of the second Ga-Sb bond length in the top substrate layer reported by van Gemmeren *et al.* (and listed in Table VII). We found all Ga-Sb bonds to be essentially the same length with a value close to our theoretical bulk bond length of 2.60 Å, in accord with the concept of bond-length conservation, a point already made in many previous works for the clean surface, other III-V(110) substrates with a Bi adsorbate and the (1×1) reconstructions in this paper.

Tables V, VI, and VII also show certain structural quantities obtained by us for the combined EOTS and ECLS model that correspond more or less to those presented for the modified ECLS model. It is certainly unlikely that such a structure could be consistent with the measurements of van Gemmeren *et al.* Key differences between the two structures lie obviously in the Bi overlayer region. Whereas the modified ECLS gave rise to two different Bi chain tilt angles, they were very close to each other in size and indeed, van Gemmeren *et al.* only quoted the one value. The combined ECLS-EOTS has two vastly differing tilt angles, one which is just a few degrees off horizontal, and one which is just slightly larger than the larger of the two obtained for the modified ECLS. The distortion in the substrate is quite different for the two models. The vertical buckling $\Delta_{\perp 5}$ of the (remaining) top layer substrate chain for the modified ECLS is only about a quarter of the average buckling of the top layer substrate chains (i.e., average of $\Delta_{\perp 4}$ and $\Delta_{\perp 5}$) for the combined ECLS-EOTS. For both (1×2) models this buckling is much larger than for the (1×1) ECLS or EOTS model. The unexpected substantial substrate relaxation obtained in our work for the combined ECLS-EOTS means that this model cannot be disqualified on the basis of core-level shift measurements alone.[10] While the buckling of the individual second substrate layer chains ($\Delta_{\perp 7}$ and $\Delta_{\perp 9}$) is similar for the two models, there is a significantly larger vertical separation between the two chains ($\Delta_{\perp 8}$) for the combined ECLS-EOTS than for the modified ECLS. Interestingly, the values for $\Delta_{\perp D}$, corresponding to the vertical separation between the highest lying Bi and the bottom of the surface valley, are very close to one another for the two models. Despite these differences, the various calculated bond lengths for the two models are very close to each other.

3. Band structure

The band structures obtained for the two structural models are quite different. The combined EOTS and ECLS ($M2$ model) gives rise to a semimetallic situation with the surface conduction states penetrating below the bulk valence-band maximum at the zone boundaries. The modified ECLS, however, does produce a semiconducting band structure, with the fundamental band gap almost clear of any surface states, with the lowest surface conduction state only just penetrating the fundamental band gap.

Figure 8 shows our electronic band structure for the modified ECLS along with the data from Fig. 6 in Ref. 11 transposed upon it. The lowest two occupied bands correspond to the lowest band for the ECLS (1×1) and result from the combined effects of folding [due to doubling of periodicity along the [001] direction with respect to the (1×1) ECLS] and the modified ECLS chain geometries. The lowest of these two bands is essentially the Bi-Bi $ss\sigma$ bonding state of

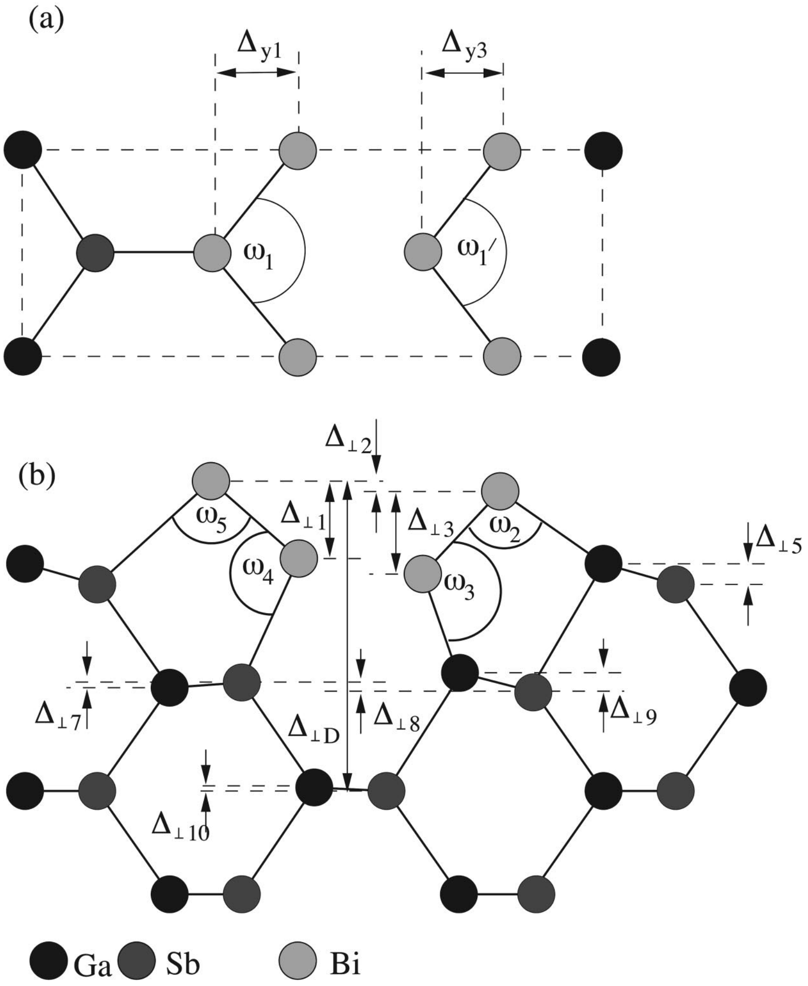

FIG. 6. Schematic diagram of modified ECLS model proposed by vam Gemmeren *et al.*

the Bi chain bonded to Sb atoms only. However, along the $\bar{M}/2$ segment this band becomes degenerate with one coming out of the valence continuum. This doubly degenerate nondispersive state is now more Bi-Sb $ss\sigma$ bondinglike. These two bands correspond to the lowest surface state for the ECLS (1×1) phase. The higher of these two states is also essentially the Bi-Bi $ss\sigma$ bonding state of the Bi chain bonded to Ga. Again this band becomes degenerate with another along the $\bar{M}/2$ segment. In this region, the state becomes Bi-Ga *s* bonding like, and also takes up a significant Sb *s*-like character from the substrate. These two states correspond to the second lowest occupied surface state for the ECLS (1×1) phase.

The two states seen in the lower part of the ionicity gap correspond to the third state for the ECLS (1×1), and are the antibonding counterparts of the two states seen below the the valence-band continuum. At the $\bar{\Gamma}$ point the lower of the two is localized on the Bi chain bonded to Ga and the higher on the Bi chain bonded to Sb, with a splitting consistent with the folding of the analogous state from the ECLS band structure. However, along the $\bar{\Gamma}\rightarrow\bar{X}'/2$ direction, the two bands split considerably in energy, interacting such that both bands have components on the Bi atoms of each chain.

Due to the folding of the bands for the (1×2) reconstruction there is no stomach gap at and around the zone boundary at $\bar{X}'/2$. However, the state for the ECLS (1×1) geometry maintains its energy location at the upper end of the stomach gap at and around the $\bar{M}/2$ corner of the surface Brillouin zone. This state agrees very well near $\bar{X}$ with the ARUPS data reported by McIlroy *et al.* The localization of this state is not straightforward, but is essentially similar to the stomach gap state observed for the ECLS structure, localized on the lower Bi-Sb pair of the Bi chain bonded to Sb.

Along the $\bar{M}/2\rightarrow\bar{X}$ direction there are two flat bands just above the top valence-band edge. A similar state is also seen for the ECLS (1×1) geometry. The energy location of these two bands has excellent agreement with the highest state identified from the ARUPS data. It is possible that the state detected by ARUPS was in fact two states very close to one another that were difficult to resolve. Along the $\bar{\Gamma}\rightarrow\bar{X}'/2$ direction we have calculated a flat band, again in excellent agreement with the ARUPS data. The dispersion of this band can be readily differentiated from the similar band for the ECLS (1×1) geometry, which is more dispersive. We find the bandwidth of the highest occupied state to be about 0.7 eV for the (1×2) phase and and 1.0 eV for the (1×1) phase. This is very close to the experimentally determined values of 0.83 and 1.09 eV, respectively.[11] The two bands that we observe in the gap region are essentially localized on the lone pairs of the Bi atoms, and as such have most in common with the highest occupied state of the ECLS band structure. However, we are able to compare the localization of the highest occupied state at the $\bar{X}$ point directly with that

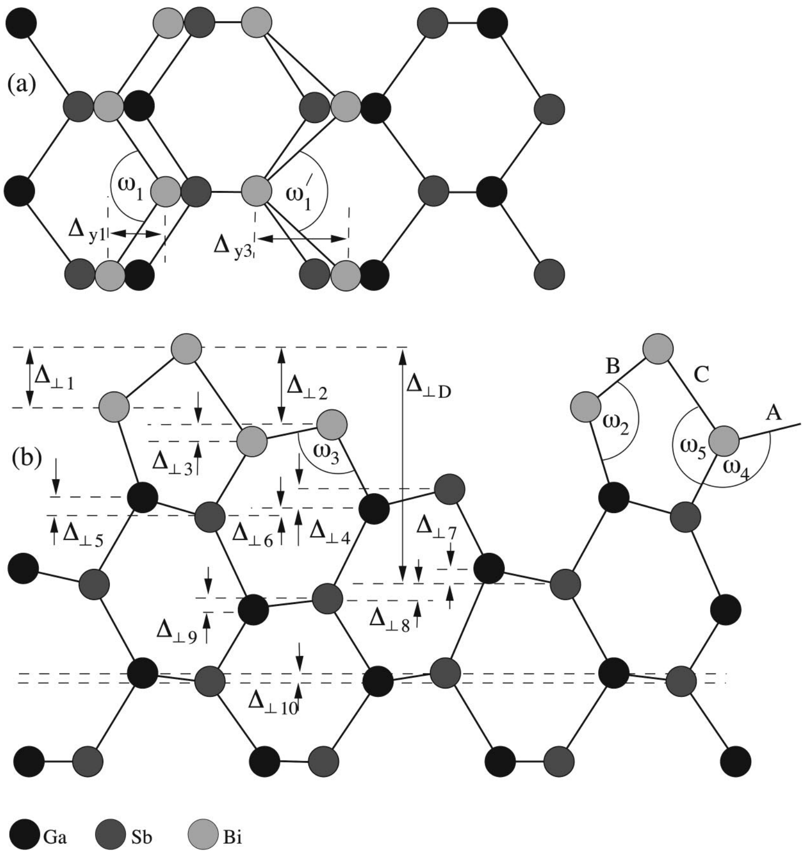

FIG. 7. Schematic diagram showing our relaxed geometry for the combined ECLS-EOTS structure indicating certain calculated parameters. Bonds are recognized as A, ECLS-like, B, EOTS-like, and C, link. (See Table VII.)

for the ECLS bands at the $\overline{X}$ point, since this point is not affected by folding effects. As was the case for the ECLS, this band is highly localized on a Bi atom bonded to Ga. In this case it is associated with the p_z orbital of the higher-lying Bi atom of the chain bonded to Ga.

On the basis of our investigations we therefore suggest that whereas the experimentally determined band structure of McIlroy *et al.*[11] was found to be inconsistent with the combined EOTS and ECLS model that they propose, their measurements do yield excellent agreement with the structural model put forward by van Gemmeren *et al.*

IV. ENERGETIC COMPARISON BETWEEN THE TWO (1×2) MODELS AND THE ECLS

The calculations for the modified ECLS and the combined ECLS and EOTS models containing a different number of atoms means that the two cells may not be energetically compared directly. In order to be able to make the link between the energy of the two structures one must consider the chemical potential of the GaSb substrate. We have calculated a value for μ_{GaSb} equal to -15.609 ± 0.001 Ry.

The two (1×2) supercells differ in composition by two GaSb pairs. That is, in order to compare the energy of the modified ECLS geometry with the combined ECLS-EOTS geometry, one should add $2\mu_{\mathrm{GaSb}}$ to the total energy of the modified ECLS geometry. This leads to an energy that is 1.5 eV lower than the combined ECLS-EOTS geometry. This tells us that the modified ECLS geometry is 0.75 eV per (1×2) surface unit cell energetically more favorable than the combined ECLS-EOTS geometry. This very significant energy difference is further reason to support the opinion held by van Gemmeren *et al.* that the GaSb(110)(1×2)/Bi(1 ML) reconstruction is accounted for by their modified ECLS model.

However, it is worth comparing the energy of these two (1×2) reconstructions with that of the original (1×1) ECLS. By augmenting the (1×1) ECLS geometry to a (1×2) unit cell and repeating the total energy calculation we are able to compare the energies between the ECLS and combined ECLS and EOTS directly, and between the ECLS and modified ECLS through the chemical potential.

The (1×2) augmented ECLS calculation yields a total energy that is lower than that of the combined ECLS-EOTS by 0.73 eV per (1×2) surface unit cell. This tells us immediately that there is no energetic gain in the (1×1) ECLS system making the transition to the combined ECLS-EOTS. This essentially means that we can disregard this appealing

TABLE V. Angular separations as defined in Figs. 6 and 7. All values are in degrees.

	ω_1	ω_1'	ω_2	ω_3	ω_4	ω_5	ω_{t1}	ω_{t3}
Modified ECLS	90.3	90.7	97.8	102.3	99.8	101.1	33.4	38.4
ECLS-EOTS	90.0	92.4	104.1	101.3	96.6	116.0	39.5	6.8
X-ray diff. (Ref. 13)	90±2	90±2	≈100±1	≈100±1	≈100±1	≈100±1	34±3	34±3

TABLE VI. Relative atomic displacements for the GaSb(110)(1×2)/Bi(1 ML) phase as defined in Figs. 6 and 7. All values are in Å.

	Δ_{y1}	Δ_{y3}	$\Delta_{\perp D}$	$\Delta_{\perp 1}$	$\Delta_{\perp 2}$	$\Delta_{\perp 3}$	$\Delta_{\perp 4}$	$\Delta_{\perp 5}$	$\Delta_{\perp 6}$	$\Delta_{\perp 7}$	$\Delta_{\perp 8}$	$\Delta_{\perp 9}$	$\Delta_{\perp 10}$
Modified ECLS	1.76	1.64	5.86	1.16	0.05	1.30		0.10		0.01	0.10	0.16	0.02
ECLS-EOTS	1.59	2.01	5.94	1.30	1.64	0.24	0.45	0.35	0.15	0.02	0.18	0.12	0.06
X-ray diff. (Ref. 13)	1.71	1.70	6.12	1.29	0.0	1.34		0.0		0.17	0.17	0.17	0.0

structure all together. On the other hand, the energy difference between the (1×2) augmented ECLS and the modified ECLS favors the latter, but by only about 0.02 eV. Ideally, we would require a larger energy difference to be able to safely predict that the modified ECLS was preferential to the ECLS structure.

V. DISCUSSION

The first part of this study confirmed that the ECLS was the lowest energy structure for the (1×1) phase of the Bi/GaSb(110) system. It did however show that it was different to the ECLS for other Bi/III-V(110) systems in that the tilt of the Bi chain was smaller for a GaSb substrate and that the tilt of the Bi chain was in the opposite direction. It has been postulated that two properties contribute to this observation. The first is that since Sb and Bi have similar electronegativities, the Bi atom bonded to the substrate anion experiences less of a pull than it does from the more electronegative anions encountered in previous studies. Second, for GaSb the cation is smaller in size than the anion whereas for most of the other III-V(110) substrates studied it is the other way around. One substrate that would have the same ratio as GaSb is AlSb since Al and Ga have similar atomic radii. However, Al is much less electronegative than Ga, an effect that might also determine the nature of the tilt.

If one were to consider an InSb(110) substrate that also disfavors a (1×1) reconstruction then the first difference would hold, but not the second since In atoms are larger than Sb atoms. As such we might expect the Bi tilt on such a substrate to be in the same direction as that on GaAs, InP, and InAs(110) substrates due to the relative atomic sizes of the substrate atoms, but very much smaller in angle due to the similar electronegativities of Bi and Sb. Preliminary calculations support this prediction, but further investigations are required to address the nature of the tilt as a function of the substrate. Such a study might prove useful in gaining a better insight into the reasons why Bi/GaSb(110) and Bi/InSb(110) prefer higher order reconstructions and whether this is also true for other Bi/III-Sb systems. If these systems are indeed different because the anion has a similar electronegativity to the adsorbate species, then one might expect Sb/III-Sb systems to behave in a similar fashion. However, Ford *et al.*[16] were unable to deposit Sb epitaxially on either GaSb(110) or InSb(110). This would further suggest that the particular relationship between the cation and adsorbate electronegativities could be crucial in determining the physics of the resulting surface. However Bi on InAs(110) behaves very similarly to Bi on GaSb(110) in terms of the reconstruction domain sizes and their temperature dependence. This would suggest that the substrate lattice parameter is the main contributor into deciding whether a full epitaxial (1×1) layer is stable or not upon annealing since InAs and GaSb have very similar lattice parameters.

Our modified ECLS results were very satisfactory indeed. However, there are a few points that merit further discussion. The main differences that arise between our results and the x-ray diffraction results are that our Bi-Ga bonds were significantly shorter than the x-ray diffraction results and that our two Bi chains were more different to one another than those reported by x-ray diffraction measurements. The Bi-Ga bond lengths that we obtained for the (1×2) modified ECLS were very close to those that we obtained for the simple (1×1) ECLS, which were also in good agreement with the x-ray diffraction results for the (1×1) ECLS. This discrepancy is consistent with identical tilts reported by van Gemmeren *et al.* for the two Bi chains of the modified ECLS which we found to be different from one another. The Bi-Ga bond length reported in Refs. 13 and 17 are quite close to the Bi-Sb bond length and as such lead to more symmetry between the two Bi chains. It is possible, therefore, that the model used by van Gemmeren *et al.* does not permit enough asymmetry between the two Bi chains, hence evening out the tilt of the two chains and increasing the length of the Bi-Ga bonds. However, such differences are only minor and agreement between both theoretical and x-ray diffraction results is so good as to give very strong support to this model.

One final question arises, and that is that of the stability of

TABLE VII. Selected bond lengths in Å for the GaSb(110)(1×2)/Bi(1 ML) phase.

	Bi-Bi	Bi-Ga	Bi-Sb	Ga-Sb
Modified ECLS	2.98 (Bonded to Ga)	2.64	2.86	2.59 (Top)
	2.99 (Bonded to Sb)	2.66	2.89	
ECLS-EOTS	2.94 (ECLS)	2.68 (ECLS)	2.84	2.59 (Top)
	2.96 (LINK)	2.69 (EOTS)		2.57 (Top)
	3.00 (EOTS)			
van Gemmeren *et al.*	3.06 (Bonded to Ga) (Ref. 17)	2.79±0.08	2.87±0.07	2.57±0.06
[X-ray diff (Ref. 13)]	3.04 (Bonded to Sb) (Ref. 17)	2.87±0.08	2.96±0.08	2.77±0.07

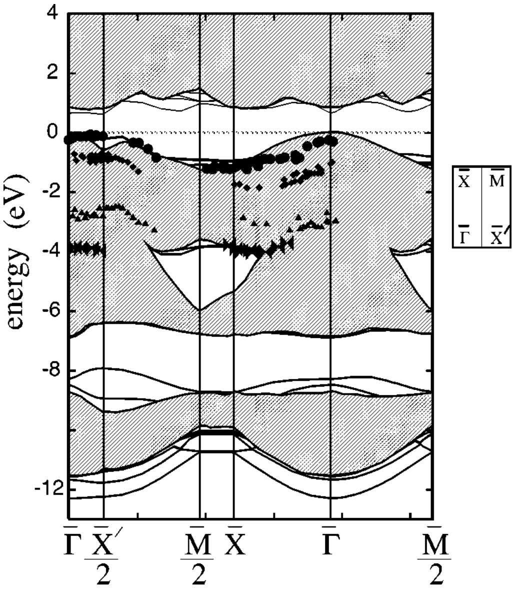

FIG. 8. Band structure for GaSb(110)(1×2)/Bi(1 ML) with modified ECLS termination. Hatched regions show bulk-projected band structure for GaSb(110)(1×2). Occupied surface states are shown as thick lines and unoccupied surface states are shown as thin black. ARUPS data reported by McIlroy *et al.* are shown as circles, squares, lozenges, triangles, and bow ties.

the (1×2) structure over the (1×1). We saw in Sec. IV that the energetic difference is very small indeed, at only about 0.02 eV. This in itself would not be enough to give strong support for the relative stability. However, the loss of the Ga-Sb chain on annealing makes the process irreversible as was found by Ford *et al.*[16] van Gemmeren and co-workers[13,17] argue most reasonably that the main driving force behind the change in a reconstruction is an attempt to improve the size of the bond angles that the Bi chains make with the substrate. The extent to which Bi bond angles for the (1×1) are unfavorable is determined by the extent to which the substrate constrains these overlayer chains. In order to improve the geometry close to the interface between the overlayer and top substrate layers, the substrate has to distort considerably. In order to relieve some of this strain, missing substrate rows are formed, leading to the modified ECLS with an associated redistribution of electronic charge between the two Bi chains. This can account for what is only a small energy gain in going from the (1×1) to (1×2) structure. There is a definite energy gain in improving the relative orientation of the Bi-Bi and Bi-substrate bonds, but this is largely cancelled by the increased strain in the substrate and charge redistribution. The stability therefore comes from the irreversible nature of the process by which the surface loses the Ga-Sb rows.

VI. CONCLUSIONS

In the case of the simple GaSb(110)(1×1)/Bi(1 ML) system, we have given support to the view held by van Gemmeren *et al.* that the surface is described by the ECLS model. We have shown that this structure is more favorable than its main rival, the EOTS model. Our geometric results are in excellent agreement with those obtained by x-ray diffraction. The tilt of the Bi chain was found to be much smaller and in the opposite direction to that obtained for Bi on other substrates containing As and P as the anion. Furthermore, we present an electronic band structure, which is in good agreement with the ARUPS results of McIlroy *et al.* for the (1×1) reconstruction of the GaSb(110)(1×1)/Bi(1 ML) surface, and confirm that the two highest surface states for this system are localized on the adsorbate layer only. The orbital nature of these surface states have also been determined. In agreement with McIlroy *et al.*, we find that the two highest occupied states are strongly localized on the Bi chain, in contrast to these states on previously studied substrates containing As or P anions.

For the stable GaSb(110)(1×2)/Bi(1 ML) phase, we have explored a number of different possible structures and have concluded that the best candidate is the modified ECLS structure reported by van Gemmeren *et al.* For this model, our calculated structural pararmeters agree very well with those obtained by van Gemmeren *et al.* Furthermore, the substrate distortions for this model differ considerably from those for the combined ECLS-EOTS, despite sharing similar values of bond lengths. Our band-structure calculations for the modified ECLS showed excellent agreement with the ARUPS data presented by McIlroy *et al.* The band width reduction of the highest occupied state upon the (1×1) →(1×2) phase transition obtained theoretically agrees with experiment. The orbital nature of the surface states was also determined, and could be understood in terms of originating from their analogous states for the (1×1) reconstruction.

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