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# Sb-induced GaAs(111)B surface reconstructions: success and failure of the electron-counting rule

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**Abstract**

Deposition of antimony on the GaAs(111)B-(2 × 2) surface, followed by annealing in the 300–525°C range, results in reconstructions having Sb trimers and Sb chains as their basic structural units. Scanning tunnelling microscopy data illustrates that a transition from a complex surface terminated by a number of local arrangements of Sb chain pairs and trimers to a (1 × 3) reconstruction having a high degree of long-range order occurs as the annealing temperature is increased. While the various unit cells formed by the combination of chain pairs and trimers satisfy the electron-counting rule, the unit cell of the (1 × 3) structure formed at higher annealing temperatures has partially filled dangling bonds. Some possible reasons for this observed breakdown of the electron-counting model are discussed.

*Keywords:* Antimony; Gallium arsenide; Metal–semiconductor interfaces; Scanning tunneling microscopy; Surface relaxation and reconstruction

The surface reconstructions of polar semiconductors are widely accepted to be constrained by the electron-counting rule [1]. This rule states that stable surface structures are formed when there are sufficient electrons to fill all the dangling bonds of the electronegative element but leave those of the electropositive element empty. For example, on GaAs surfaces this is achieved by a transfer of electronic charge from Ga (the electropositive element) to As. The resulting energy levels of the filled (As) and empty (Ga) dangling-bond orbitals are degenerate with the bulk valence and conduction bands. There are therefore no surface states within the bulk band-gap. To date, the structures of nearly all group III–V and II–VI surfaces have been shown to be consistent with this rule, some examples being ZnSe(001)-(2 × 1) [1], GaAs(100)-c(4 × 4) and (2 × 4) [2], GaAs(311)A-(8 × 1) [3], and GaAs(111)B-(2 × 2) [4]. A notable exception to the electron-counting rule is the GaAs(111)B-($\sqrt{19} \times \sqrt{19}$) R23.4° reconstruction, where surface Ga dangling bonds are partially filled.

Electron counting has been extended to predict possible reconstructions of adsorbed overlayers on group III–V semiconductors. Structure models for the (2 × 1) reconstructions resulting from the adsorption of group VI elements on the GaAs(001) surface have been proposed by considering electron-counting principles [5]. The surface structures formed by deposition of Si on GaAs(001) have been found to be consistent with a modified

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electron-counting model [6]. Within this model, reconstructions for which the group V dangling bonds would not be filled on undoped material are stabilised by electrons from the Si donors. Again, the critical criterion is the absence of partially filled dangling bonds.

We have recently shown that the complex family of reconstructions formed by depositing Sb on the GaAs(111)B-(2×2) surface and annealing to 375°C can be understood in terms of electron counting [7]. In this Letter we present scanning tunnelling microscopy (STM) data on the changes in structure that occur as the Sb-terminated GaAs(111)B surface is annealed at higher temperatures. A transition from reconstructions having short-range order but obeying the electron-counting rule to a long-range ordered (1×3) reconstructed surface whose unit cell has a partially filled dangling bond occurs. This result shows that the electron-counting rule is not always the dominant driving force behind the formation of adsorbate-induced reconstructions.

Clean (2×2) reconstructed GaAs(111)B surfaces were prepared by thermally desorbing a protective As cap from a molecular beam epitaxy (MBE) grown GaAs buffer layer. Details of the growth and As capping procedure are given elsewhere [8]. STM images showed that the resulting GaAs(111)B-(2×2) surface [9] was of comparable quality to MBE-grown samples that have been investigated in situ [4]. Sb was deposited on the (2×2) surface, which was held at room temperature during the deposition, from a Knudsen cell operating at a temperature of 410°C. The STM data were acquired using a commercially available system from W.A. Technology, Cambridge, UK. Electrochemically etched W tips that were cleaned by electron-bombardment heating in situ were used.

The (2×2) reconstruction of the GaAs(111)B surface consists of As trimers bonded to an underlying unreconstructed As layer [4]. This double As layer termination results in all Ga atoms being four-fold or bulk coordinated and, therefore, having no dangling bonds. Within the electron-counting model there are thus no electrons present that may be transferred from Ga to As. However, the second-layer As atoms bonded to the first-layer trimers transfer their excess electronic charge to the remaining As atoms not involved in bonding to the trimer. This results in all As dangling bonds being filled, and electron counting is satisfied.

Deposition of submonolayer coverages of Sb on the (2×2) surface followed by annealing at 300°C gives rise to regions of Sb-induced (2×2) reconstruction. (The interaction of Sb with the GaAs(111)B surface following annealing at lower temperatures is described in Ref. [9]). This Sb-induced (2×2) reconstruction arises from the replacement of the first-layer As trimers by Sb trimers [7]. Fig. 1 illustrates that the Sb trimers, although having local (2×2) periodicity, are somewhat disordered when compared to the clean GaAs(111)B-(2×2) surface.

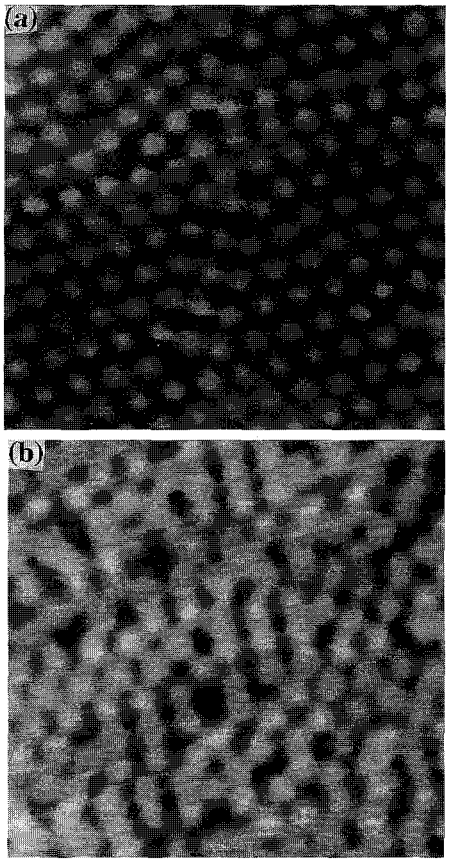



Fig. 1. 98 Å×98 Å filled-states images (−3.0 V, 100 pA) of (a) the clean GaAs(111)B-(2×2) As trimer reconstruction, and (b) the more poorly ordered Sb-induced (2×2) reconstruction.

The observation of a trimer-based $(2\times2)$ unit cell following replacement of As with Sb is completely consistent with the electron-counting rule. As the number of available electrons remains the same following the replacement of one group V element by another, the surface would be expected to reconstruct in a similar manner. A similar situation arises on GaAs(001) where, following Sb adsorption and annealing, a reconstruction with the same $(2\times4)$ periodicity as the clean As-terminated surface results [10]. However, as noted above for GaAs(111)B, STM images show that there are significant differences in the ordering of the Sb- and As-terminated surfaces although the reconstruction periodicities are identical [11]. These differences in ordering highlight the fact that mechanisms other than electron counting influencing energy minimisation should not be overlooked. In the present case, the higher degree of disorder observed for the Sb-induced $(2\times2)$ reconstruction may be related to the difference in covalent radii of Sb and As. The increase in bond distortion induced by the larger Sb atom bonded in the trimer structure may prohibit the formation of a well-ordered $(2\times2)$ reconstruction.

Following annealing of the Sb-terminated surface at higher temperatures (375°C) reconstructions are observed which are not formed on clean As-terminated GaAs(111)B (see Fig. 2a). The most striking feature of this image is the large number of Sb chain pairs with local $(1\times3)$ ordering that cover the surface. Between these chain pairs are various arrangements of Sb trimers. It is important to stress two points. First, the Sb chain and trimer structures are chemisorbed on an underlying As layer [7]. In addition, we have previously discussed how the various unit cells formed by the combination of chain pairs and trimers conform to electron counting [7,9]. For example, a region exhibiting local $(3\times8)$ order is identified in Fig. 2a, with the atomic structure model derived by considering electron counting shown in Fig. 2b.

It is evident that the reconstructions observed in Fig. 2a have Sb chain pairs as their basis. If we consider solely the electron-counting model there is no driving force behind the formation of Sb chains. As mentioned above, a $(2\times2)$ reconstruction with Sb trimers replacing As trimers ensures


(b)

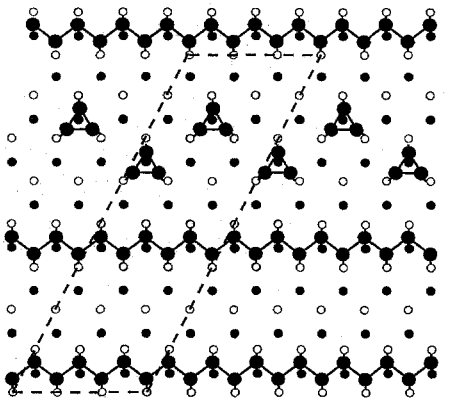
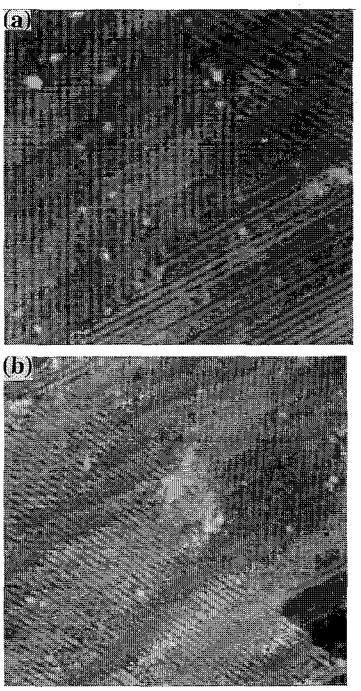


Fig. 2. (a) 195 Å × 195 Å scan of the GaAs(111)B surface following deposition of 3 ML of Sb and annealing at 375°C. A number of reconstructions having Sb trimers and chains as their structural units are visible in the image. A region of $(3\times8)$ reconstruction is outlined. (b) Ball-and-stick model of the GaAs(111)B:Sb-$(3\times8)$ reconstruction. Large filled circles represent Sb atoms, small open circles As atoms, and small filled circles Ga atoms.

that all group V dangling bonds are filled. Therefore, although the complex surface reconstructions observed in Fig. 2a are consistent with electron counting, another factor drives the formation of Sb chains (and chain pairs).

At higher annealing temperatures there is a transition from locally ordered trimer- and chain-based structures to a $(1\times3)$ reconstruction having

long-range order. Figs. 3a and 3b are filled-state images of the Sb-terminated surface after annealing at 475°C and 525°C, respectively. It is clear from the images that a transition from locally ordered Sb chain pair and trimer structures to a $(1\times3)$ reconstruction consisting of a uniform coverage of Sb chains occurs as the annealing temperature is increased. Some small isolated regions of trimer-terminated surface remain, but typically cover areas of no more than 50 Å × 50 Å. We observe three equivalent domains of $(1\times3)$ structure as expected considering the symmetry of the (111) substrate. Referring to the ball-and-stick model of the $(1\times3)$ reconstruction shown in Fig. 3c, while the Sb atoms bonded in the chain structure will have filled dangling bonds, the remaining second-layer As atom not bonded to Sb in the unit cell will be electronic-charge deficient. This partially filled dangling bond will have an energy within the bulk band-gap, rendering the $(1\times3)$ structure unstable from the electron-counting point of view. As we observe a well-ordered $(1\times3)$ surface, it is clear that the electron-counting method has broken down and an alternative mechanism of surface energy minimisation dominates the formation of the reconstruction.




(c)

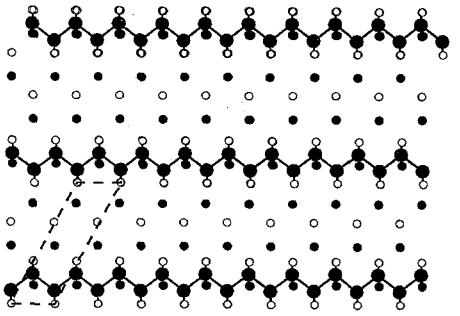


Fig. 3. (a) 410 Å × 410 Å image of GaAs(111)B:Sb following annealing at 475°C. (b) 530 Å × 530 Å image following subsequent annealing at 525°C. Although some surface damage due to an accidental tip crash is visible near the centre of the image, it is clear that the surface is predominantly terminated by a uniform coverage of Sb chains. (c) Ball-and-stick model of the GaAs(111)B:Sb-$(1\times3)$ reconstruction. Large filled circles represent Sb atoms, small open circles As atoms, and small filled circles Ga atoms.

It is well established that the extent of local surface and subsurface bond distortion plays a large role in determining the nature of the surface reconstructions on elemental semiconductor surfaces (the Si(111)-$(7\times7)$ and Ge(111)-c$(2\times8)$ structures in particular) [12,13]. Extending this argument to group III–V surfaces, as discussed by LaFemina [14], there will be a balance between the drive towards attaining charge neutrality and the resulting distortion of bond angles and bond lengths. We suggest that for the Sb-terminated GaAs(111)B surface, the chain configuration of Sb bonding minimises adsorbate-induced distortion of bonds and is therefore lower in energy.

It proves interesting to compare our results for GaAs(111)B:Sb to bonding within the bulk Sb crystal and Sb adsorption on GaAs(110) [15,16]. In the GaAs(110) case Sb chains also form, but due to the $(1\times1)$ reconstruction of the non-polar substrate, electron counting is satisfied. An intrachain Sb bond angle of 91° has been calculated, which indicates a $p^2$ bonding within the chain [15]. We have previously used the bulk Sb–Sb bond length in considering the Sb–Sb intrachain bond angle for double chains on

GaAs(111)B:Sb [7]. However, as noted by LaFemina et al. [15], the sum of the Sb covalent radii (2.72 Å) represents a slightly better estimate of the bond length when considering an adsorbed Sb overlayer on GaAs. Using this value and the spacing of As atoms on the GaAs(111)B surface (4 Å), we can determine geometrically that the Sb–Sb intrachain bond angle is 94.7°. This value is close to both the bulk Sb–Sb bond angle of 96.5° and the intrachain Sb bond angle on GaAs(110). We conclude that the formation of an Sb chain structure is due to reduction in bond distortion dominating surface energy minimisation. Furthermore, by using a similar argument to that above, the value of the bond angle within an As–As chain on the GaAs(111)B surface would be much greater than the As–As bulk bond angle. The formation of As chains is therefore unfavourable from both the electron counting and bond distortion viewpoints.

A phase transition of relevance to our study is the $(2\times2)$ to $(\sqrt{19}\times\sqrt{19})$ R23.4° reconstruction change that occurs following annealing of the GaAs(111)B surface above 500°C. In that case the electron-counting rule also fails to account for the formation of the $(\sqrt{19}\times\sqrt{19})$ reconstruction. The phase transition is driven by the desorption of approximately 1.1 ML of As from the $(2\times2)$ surface [4]. For the $(3\times8)$ structure model shown in Fig. 2b (and all other Sb-terminated GaAs(111)B reconstructions that obey electron counting [7]) the Sb coverage is 0.75 ML. However, for the $(1\times3)$ reconstruction (Fig. 3c) the coverage is lower (0.66 ML). Therefore the formation of the $(1\times3)$ reconstruction may also be due to the desorption of surface atoms. It should be noted that it is not possible to fulfil electron counting with an Sb coverage of 0.66 ML adsorbed on a complete, unreconstructed As layer.

Alternative structure models, other than that shown in Fig. 3c, may be considered for the $(1\times3)$ reconstruction. One possibility is that the reduction in first-layer Sb may not be due to Sb desorption but a replacement of 0.11 ML of second-layer As by Sb. Note that this replacement would not affect electron counting, and the $(1\times3)$ unit cell would remain 1/4 electron deficient. A second possibility is that desorption of second-layer As (between Sb chains) occurs. Consider a $(1\times3)$ unit cell in which the second-layer As atom between the chains has been removed. This results in the formation of three Ga dangling bonds. There is then an excess of $(3\times3/4)$ electrons, from the Ga dangling bonds, plus $(2\times1/4)$ electrons, from the second-layer As atoms bonded to the Sb chain (i.e. 11/4 electrons). It would be possible to fulfill electron counting by transferring 1/4 electron to 11 neighbouring unit cells. Thus electron counting could be satisfied by desorbing 1/12 ML of second-layer As. We note, however, that intra- and interlayer charge transfer over relatively large distances would be required, and this is likely to be energetically unfavourable [17].

Two experimental observations rule out As desorption or the replacement of second-layer As by Sb in considering structure models for the chain terminated surfaces observed in Figs. 3a and 3b. First, we have observed isolated areas of $(1\times3)$ structure coexisting with regions of trimer- and chain-based reconstruction following deposition of 0.2 ML of Sb and annealing at 350°C. The desorption or replacement of second-layer As at this annealing temperature is very unlikely. This result also strengthens the argument that the local surface Sb coverage plays a role in the formation of the $(1\times3)$ reconstruction. There is also little change in the Ga 3d or Sb 4d core-level photoemission spectra from the Sb-terminated surface in the annealing range used in our study [18]. Large changes would be expected if either As desorption or replacement was occurring.

We therefore believe that the most plausible structure for the chain-terminated surface is the $(1\times3)$ unit cell shown in Fig. 3c, and that the thermal desorption of Sb plays a large role in the transition of the surface to a solely chain-based reconstruction. It is interesting to note that for other group III–V semiconductor surfaces, for example GaAs(001) [19], reduction of the group V element surface concentration does not lead to reconstructions failing to satisfy the electron-counting rule.

It should be noted that the electron-counting rule implicitly assumes that both Ga and As dangling bonds are $sp^3$ hybridised [1]. Recent studies have suggested that rehybridisation of the dan-

gling-bond orbitals may need to be considered when determining the total energy of a particular GaAs surface reconstruction [20,21]. For the GaAs(111)B-($\sqrt{19} \times \sqrt{19}$)R23.4° phase, the Ga atoms are two-fold coordinated, and their bonding might therefore be expected to differ from being purely $sp^3$ in character. It is possible that rehybridisation has occurred on the GaAs(111)B:Sb-($1 \times 3$) surface; however, the same structural unit (Sb chain) appears in the ($3 \times 8$) reconstruction formed at lower temperature which does conform to electron counting. A tight-binding, total-energy minimisation calculation might provide some insight into the bonding of the Sb chains to the GaAs(111)B substrate.

In conclusion, we have observed the breakdown of the electron-counting model for the GaAs(111)B:Sb system. We propose that the principal factor controlling the formation of Sb chains is that the Sb–Sb and Sb–As bonding within the chains minimises adsorbate-induced bond distortion. The transition of the surface from trimer- and chain-based reconstructions to being predominantly chain-terminated is driven by the desorption of Sb atoms.

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