

# Cation-rich (100) surface reconstructions of InP and GaP

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The trimer reconstruction of the (100) InP surface which has been discovered experimentally is confirmed by first-principle calculations. The charge density of atomic configuration, which has the lowest surface energy is in perfect agreement with experimental scanning tunneling microscopy images. We predict the same trimer reconstruction also to be observable on GaP (100) surfaces and discuss how local stress makes this reconstruction energetically unfavorable for GaAs. [S0163-1829(99)01943-8]

GaAs is considered a prototypical III-V semiconductor. As such, the observed surface reconstructions on GaAs are also expected to occur on other III-V semiconductors. Indeed, there exist general rules<sup>1-3</sup> that govern the reconstruction patterns of III-V semiconductors, which are, more or less, material independent. In the cation (i.e., group-III atom) rich (CR) regime, for example, the general rule is that the surface structure with the lowest energy is the one with the lowest surface reconstruction parameter (SRP),<sup>3</sup> which is defined as the sum of the number of anion dangling bonds  $N_a$ , and anion dimers  $N_{a-a}$ ,

$$\text{SRP}_{\text{CR}} = N_a + N_{a-a}. \quad (1)$$

Naively then, all III-V semiconductors are expected to reconstruct under cation-rich conditions with a  $(4 \times 2)$  periodicity showing only dimer related patterns, because on GaAs (Ref. 4) a  $\beta 2(4 \times 2)$  reconstruction ( $\text{SRP}_{\text{CR}} = 4$ ) is observed. All the more astonishing therefore, were the findings by MacPherson *et al.*<sup>5</sup> who performed scanning tunneling microscopy (STM) studies of the InP (100) surface, showing that under cation rich conditions the surface reconstruction involves a *trimer* unit with a  $(2 \times 4)$  periodicity. More recently, Neugebauer *et al.*<sup>6</sup> predicted GaN (in the zinc-blende structure) to reconstruct under cation-rich conditions with a  $(1 \times 4)$  *tetramer* reconstruction pattern. On the other hand, under anion (i.e., group-V atom) rich conditions the (100) surfaces of III-V semiconductors have reconstruction patterns that are all very similar.<sup>7</sup>

In this paper, we discuss why different reconstruction patterns occur under cation-rich conditions, and why almost no variation in the reconstruction scenario occurs under anion rich conditions. We show that the trimer reconstruction is not observed on a GaAs (100) surface because local surface stress causes this reconstruction to be energetically unfavorable. Moreover, we predict the trimer reconstruction also to be observed on a GaP (100) surface.<sup>8</sup>

To support our analysis we perform *ab initio* calculations for a variety of different surface reconstructions. The surface

energies were calculated using a density-functional theory<sup>9</sup> pseudopotential total energy approach.<sup>10</sup> The local-density approximation was applied to the exchange-correlation energy-functional<sup>11</sup> and the atoms were described by fully separable norm-conserving *ab initio* pseudopotentials.<sup>12</sup> The wave functions were expanded in plane waves with an energy cutoff of 10 Ry. The electron density was calculated using special **k**-point sets<sup>13</sup> with a density equivalent to 64 **k** points in the entire (100)  $(1 \times 1)$  surface Brillouin zone. The surface energy is defined as

$$E_{\text{surface}}^{\text{tot}} - \mu_{\text{anion}} N_{\text{anion}} - \mu_{\text{cation}} N_{\text{cation}}, \quad (2)$$

where  $E_{\text{surface}}^{\text{tot}}$  is the calculated total energy of the surface,  $\mu$  is the chemical potential, and  $N$  is the total number of anion or cation atoms. Experimentally, the value of the chemical potential may be varied over a certain interval. This interval may be approximated by the bulk chemical potentials of the equilibrium condensed phases of the cation and anion. These are the tetragonal structure<sup>14</sup> of In, the rhombohedral structure<sup>15</sup> of P, the trigonal structure<sup>16</sup> of As, and the orthorhombic structure<sup>17</sup> of Ga.

In Fig. 1, we show the calculated surface energies for the (100) surfaces of InP, GaP, and GaAs for a number of different cation rich reconstruction patterns. The vertical lines indicate the allowed interval of the chemical potential. For clarity, we show, in case of InP and GaAs also those anion-rich reconstructions that are lowest in energy in a more anion-rich environment. (The reconstruction scenario in the anion-rich regime is identical for InP, GaP, and GaAs.)

First, we discuss the InP surfaces. Two  $(2 \times 4)$  reconstructions were previously suggested to explain the unusual trimer reconstruction in the In-rich regime, i.e., the MacPherson model<sup>5</sup> ( $\text{SRP}_{\text{CR}} = 8$ ) and the Sung model<sup>18</sup> (MRTD) ( $\text{SRP}_{\text{CR}} = 3$ ). In accordance with the general rule, the Sung model is energetically favored over the MacPherson model. However, there are other reconstructions with a lower SRP, i.e., the mixed dimer  $(2 \times 4)$  (Refs. 19 and 20) with  $\text{SRP}_{\text{CR}}$

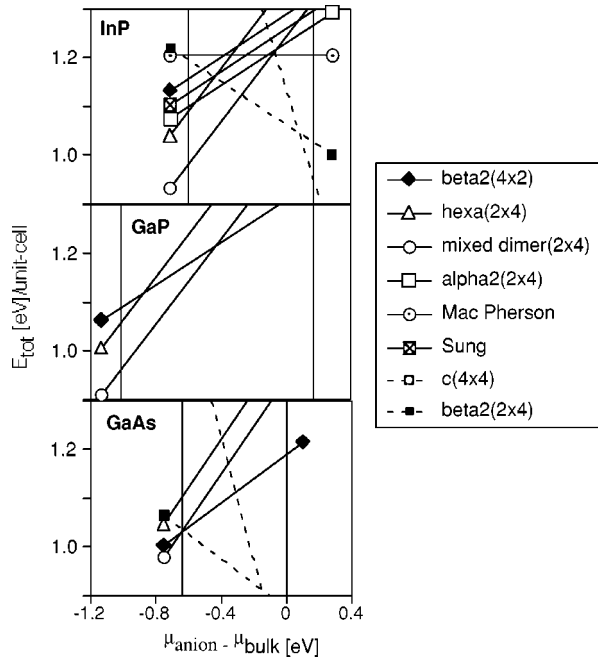


FIG. 1. The surface energy per unit cell as a function of the anion chemical potential. In the top panel we show InP, in the middle panel GaP, and in the bottom panel GaAs. The dotted lines in case of InP and GaAs are the lowest reconstructions in an anion-rich regime.

= 1 and the hexatrimer( $2 \times 4$ ) with  $\text{SRP}_{\text{CR}} = 0$ . Both of these reconstructions deserve further investigation.

We begin by focusing our attention on the hexatrimer( $2 \times 4$ ) reconstruction, which is shown in Fig. 2. In comparison to the mixed dimer model, which will be discussed later, it has two additional anion-cation bonds. It consists of one (111) surface ring (large circles in Fig. 2) on top of a (100) surface. The ring is not centered in the ideal ( $2 \times 4$ ) unit cell (dashed line), but shifted along the (110) direction. Because of this shift, the top P atom is able to bond to the underlying In atom and thereby has no dangling bonds. We thus note that despite the presence of three P atoms in the surface unit cell, this model has zero anion dangling bonds.

Also shown in Fig. 2 along with the reconstruction model are calculated STM images for InP. We computed the STM

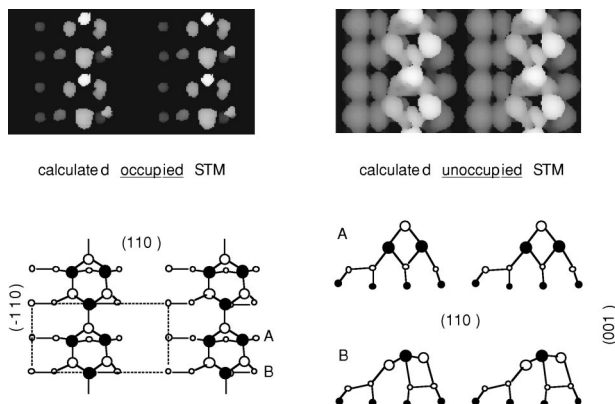


FIG. 2. The hexatrimer reconstruction: Calculated occupied and unoccupied STM image and the atomic structure, where filled (empty) circles are anions (cations).

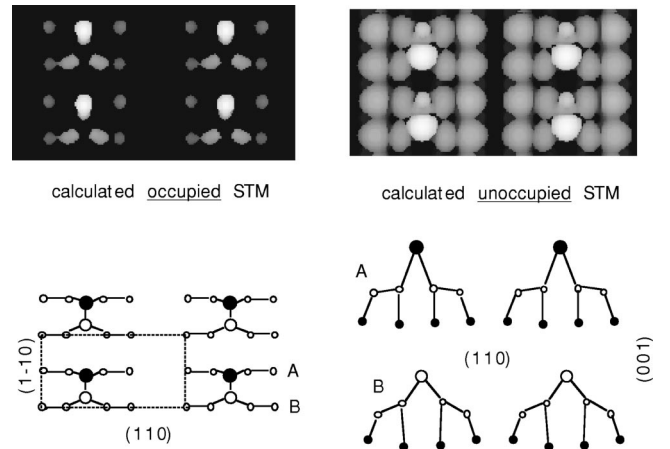


FIG. 3. The mixed dimer reconstruction: Calculated occupied and unoccupied STM image and the atomic structure, where filled (empty) circles are anions (cations).

images by calculating the charge density contour plots for different heights above the surface. Thus, the gray scale in Fig. 2 maps the height for a fixed charge density. The height interval shown is 5 Å starting from underneath the complete cation layer. The computed STM images resemble the experimental STM images except for the asymmetry. Thus, the hexatrimer is not the experimentally observed reconstruction. The top In atom of the hexatrimer( $2 \times 4$ ) reconstruction model has occupied dangling bond that gives rise to the white spot in the occupied STM (Fig. 2). Because of having this occupied dangling bond the reconstruction does not fulfill the electron counting rule, despite the fact that it is semiconducting. The top In atom forms bond angles with the neighboring three top P atoms of  $83^\circ$ ,  $106^\circ$ , and  $108^\circ$ . The average bond angle ( $99^\circ$ ) is thus smaller than the ideal tetrahedral bond angle of  $109.5^\circ$  and indicates a  $sp^3$ -like rehybridization with a filled cation dangling bond.

We believe this to be the first time a semiconducting surface reconstruction is found with an occupied cation dangling bond. Under growth conditions it is not unlikely that this hexatrimer( $2 \times 4$ ) reconstruction model may exist and be observed with STM. The surface reconstruction parameter does not include the possibility of filled cation dangling bonds. If we assume a filled cation dangling bond to be energetically twice as expensive as a filled anion dangling bond and incorporate this into the SRP the hexatrimer( $2 \times 4$ ) reconstruction would follow the general rule.<sup>3</sup>

Let us now consider the mixed dimer( $2 \times 4$ ) reconstruction found by Schmidt *et al.*<sup>19,20</sup> Its atomic model and calculated STM images are shown in Fig. 3 for InP. This reconstruction fulfills the electron counting rule and is semiconducting. In the top layer, seven anions are missing and one cation is added per ( $2 \times 4$ ) cell. The cation layer underneath is complete, but differs from the bulk geometry by six cation-cation dimers that are formed in the region of the missing anions. Altogether there are one anion dangling bond and six cation dimers. As seen in Fig. 1 it is the reconstruction with the lowest surface energy in cation-rich conditions. Therefore, it is the equilibrium structure, which will be observed in experiment.

Furthermore, the occupied charge density (Fig. 3) reveals a trimer pattern in excellent agreement with experiment.<sup>5</sup>

The trimer pattern consists of the three bright spots, which are repeated with a  $(2 \times 4)$  periodicity. The so called “head” (Ref. 5) consists of the occupied dangling bond of the top P atom, the so called “ears”<sup>5</sup> consist of the charge around the two top In dimers. The four spots around the trimer unit consist of the charge around the four lower-lying In dimers. The distance between two ears amounts to  $3.75 \text{ \AA}$ , between head and ear  $3.5 \text{ \AA}$  along the (100) direction, and the height difference between the head and ears amounts to  $0.4 \text{ \AA}$ . Experimentally, besides the trimer pattern, there was a infrequent dimer pattern observed. This is easily explained by replacing the additional top In atom by a P atom. This structure is denoted as  $\alpha 2(2 \times 4)$  ( $\text{SRP}_{\text{CR}}=3$ ) and as seen from Fig. 1 has also a low-surface energy.

Moreover, we also calculated an unoccupied STM image (Fig. 3) which, again, is in excellent agreement with the unoccupied STM image.<sup>5</sup> The unoccupied dangling bond of the top In atom gives rise to the brightest spot. The other unoccupied dangling bonds of the lower-lying In atoms give rise to the spots at the boundary of the trimer unit. The spots nearest to the top In atom are due to unoccupied states around the remaining In and P atoms.

We additionally calculated the surface energies of the hexatrimer and the mixed dimer reconstruction for GaP and compare it to that of the  $\beta 2(4 \times 2)$  reconstruction, which are all shown in Fig. 1. In the case of GaP we find a reconstruction scenario identical to InP, i.e., the  $(2 \times 4)$  structures are lower in energy than the  $\beta 2(4 \times 2)$  structure. Thus, we predict GaP to show a  $(2 \times 4)$  reconstruction pattern under cation-rich conditions. To our knowledge, there are as yet no experimental results published for the GaP (100) surface under cation-rich conditions (Ref. 8).

We performed the same analysis for GaAs. In the case of GaAs, we show the surface energy of three cation-rich reconstruction and in contrast to InP and GaP, for GaAs the  $\beta 2(4 \times 2)$  structure is lower in energy than the two other  $(2 \times 4)$  structures, despite its higher surface reconstruction parameter. As mentioned earlier, the results are in agreement with the experimental findings, where GaAs is found to reconstruct with a  $(4 \times 2)$  periodicity under cation-rich conditions.

In order to understand the difference in the reconstruction scenario between InP and GaP on one hand and GaAs on the other hand, we note that simple bond-counting arguments would predict all three materials to have similar reconstruction scenarios. The difference is due to local stress, which is neglected by simple bond-counting arguments. The main difference between both reconstructions is that the mixed dimer reconstruction includes two (inequivalent) interconnected cation dimers, whereas the  $\beta 2(4 \times 2)$  reconstruction only includes two inequivalent single cation dimers.

In Table I we show the calculated average bondlength of the cation dimers of the  $\beta 2(4 \times 2)$  and the mixed dimer reconstruction and the value of their difference. In column four, we calculated the difference in dimer bondlength between the mixed dimer and the  $\beta 2(4 \times 2)$  reconstruction. For InP this difference amounts to  $0.07 \text{ \AA}$  and for GaAs it is  $0.11 \text{ \AA}$ . Thus, the cation bonds of the mixed dimer reconstruction are most strained in case of GaAs and least strained in case of InP. Moreover, we see (column two) that the cat-

TABLE I. The next nearest-neighbor distance in bulk  $d_{\text{NN}}$ . Calculated average cation dimer bond length for the  $\beta 2(4 \times 2)$  and the mixed dimer reconstruction and their difference. The average is taken over the two inequivalent dimers for the  $\beta 2(4 \times 2)$  reconstruction and over the two inequivalent interconnected dimers for the mixed dimer reconstruction. The calculated ratio of  $d_{\text{NN}}$  and the cation dimer bond length of the mixed dimer reconstruction is a measure of the local stress.

	$d_{\text{NN}} [\text{\AA}]$	$\beta 2 [\text{\AA}]$	mix. $[\text{\AA}]$	mix. - $\beta 2 [\text{\AA}]$	$d_{\text{NN}}/\text{mix.}$
InP	4.11	2.69	2.76	0.07	1.49
GaP	3.79	2.39	2.48	0.09	1.53
GaAs	3.93	2.41	2.52	0.11	1.56

ion dimer of the GaAs  $\beta 2(4 \times 2)$  reconstruction is more strained than the corresponding dimer of GaP.

As a measure for this local stress energy one may take the ratio between the next nearest-neighbor distance (column one) and the cation dimer bondlength of the mixed dimer reconstruction (column three). The larger the ratio, the more strained are the cation dimers. We thus find for the mixed dimer reconstruction GaAs to have most strained cation dimers and InP least strained cation dimers. Thus the local stress prevents GaAs to reconstruct in the mixed dimer pattern. Since the surface reconstruction parameter of the  $\beta 2(4 \times 2)$  structure ( $\text{SRP}_{\text{CR}}=4$ ) is higher than of the mixed dimer  $(2 \times 4)$  ( $\text{SRP}_{\text{CR}}=1$ ), the exception is thus not the  $(2 \times 4)$  reconstruction of InP, but the  $(4 \times 2)$  reconstruction of GaAs.

The case of GaN is very similar to this. Recently, Neugebauer *et al.*<sup>6</sup> calculated the (100) surface of cubic GaN to reconstruct in the cation-rich regime with a  $(1 \times 4)$  tetramer pattern ( $\text{SRP}_{\text{CR}}=0$ ), which includes three interconnected Ga dimers. The lattice constant of GaN is smaller than for GaP. Thus, the stress due to interconnected cation dimers is even smaller than in case of GaP. We calculated the  $(1 \times 4)$  tetramer pattern for InP and find it to become metallic and thus energetically unfavorable. From the analysis above, we thus predict that the tetramer reconstruction will not occur for neither GaP nor GaAs.

In general, we find for cation-rich conditions, that for a fixed cation atomic radius the stress energy of reconstruction patterns involving interconnected cation dimers increases with increasing anion atomic radius. Thus the variation in surface reconstruction patterns between III-V materials is caused by the local stress energy.

As was already mentioned, there is almost no variation of (100) surface reconstructions between different III-V semiconductors under anion-rich conditions. This is understandable from two simple points of view.

First of all, the anion dimer bondlength is larger than the cation dimer bondlength. Thus, the local stress involved with the formation of anion dimers is small and therefore no variation in the reconstruction scenario occurs.

Secondly, the SRP between anion- and cation-rich conditions is different.<sup>3</sup> For cation rich conditions [Eq. (1)] the SRP is independent of the number of cations and consequently many different reconstruction patterns with varying numbers of cations may have small  $\text{SRP}_{\text{CR}}$ . Therefore differences in the constituent atomic elements become more

critical in determining the lowest energy reconstruction pattern. On the other hand, for anion-rich conditions the SRP is defined in the following way:

$$\text{SRP}_{\text{AR}} = N_a - N_{a-a} + 2N_{c-c}, \quad (3)$$

where  $N_{c-c}$  is the number of cation dimers. This is a more stringent condition. Only certain combinations of both anion and cation numbers can lead to a low  $\text{SRP}_{\text{AR}}$ . Therefore, there are only few possible anion-rich surface reconstruction patterns with a low  $\text{SRP}_{\text{AR}}$ .

In summary, we have shown that the mixed dimer recon-

struction is responsible for the unusual trimer pattern observed with STM. We predict the trimer reconstruction also to be visible on a (100) GaP surface under cation-rich conditions. The trimer reconstruction is not observed on a (100) GaAs surface, because the local stress energy involved with the trimer reconstruction is larger for GaAs than for InP and GaP. The differences in the reconstruction scenarios between III-V (100) surfaces in the cation- and anion-rich regime can be understood in terms of the surface reconstruction parameter (SRP).

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