

# Semiconductor Surface Studies

## Academic and Research Staff

Professor John D. Joannopoulos, Dr. Niko Moll, Dr. Susanne Mirbt, Dr. Pierre Villeneuve

## Graduate Students

Attila Mekis, Ickjin Park, Tairan Wang

## Technical and Support Staff

Margaret O'Meara

## Project Staff

Professor John D. Joannopoulos, Dr. Susanne Mirbt, Dr. Pierre R. Villeneuve, Attila Mekis, Ickjin Park, Tairan Wang

## 2.1. Introduction

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Understanding the properties of the surfaces of solids and the interactions of atoms and molecules with surfaces has been of extreme importance both from technological and academic points of view. The advent of ultrahigh vacuum technology has made microscopic studies of well-characterized surface systems possible. The way atoms move to reduce the energy of their surface, the number of layers of atoms involved in this reduction, the electronic and vibrational states that result from this movement, and the final symmetry of the surface layer are all of utmost importance in arriving at a fundamental and microscopic understanding of the nature of clean surfaces, chemisorption processes, and the initial stages of interface formation.

The theoretical problems associated with these systems are quite complex. However, we are currently at the forefront of solving the properties of real surface systems. In particular, we are continuing our efforts in developing new techniques for calculating the total ground-state energy of a surface system from "first principles," so that we can provide accurate theoretical predictions of surface geometries and behavior. Our efforts in this program have been concentrated in the areas of surface defects, surface reconstruction geometries, structural phase transitions, and novel computational techniques.

## 2.2. Surface Reconstructions of InP and GaP

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 that govern the reconstruction patterns of III-V semiconductors, which are, more or less, material independent. In the cation (i.e., group-II 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), 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 a  $\beta 2(4\times 2)$  reconstruction ( $SRP_{CR}=4$ ) is observed. All the more astonishing, therefore, were recent 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. 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.

In this work, we investigate 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 that the trimer reconstruction should also be observed on a GaP (100) surface.

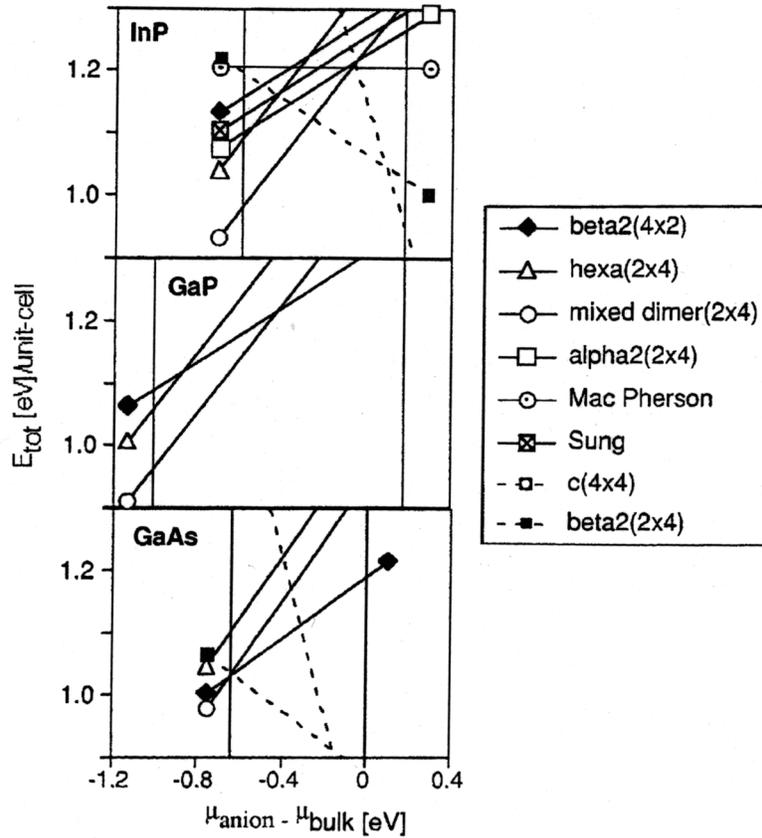


Figure 1. The surface energy per unit cell as a function of the anion chemical potential. In the top panel we show InP, in the middle panel GaP, and in the bottom panel GaAs. The dotted lines in the case of InP and GaAs are the lowest reconstructions in an anion-rich regime.

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 pseudopotential total energy approach. The local-density approximation was applied to the exchange-correlation energy-functional and the atoms were described by fully separable norm-conserving *ab initio* pseudopotentials. 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 of In, the rhombohedral structure of P, the trigonal structure of As, and the orthorhombic structure 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.

We begin by focusing our attention on the hexamer(2×4) 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 (2×4) 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.

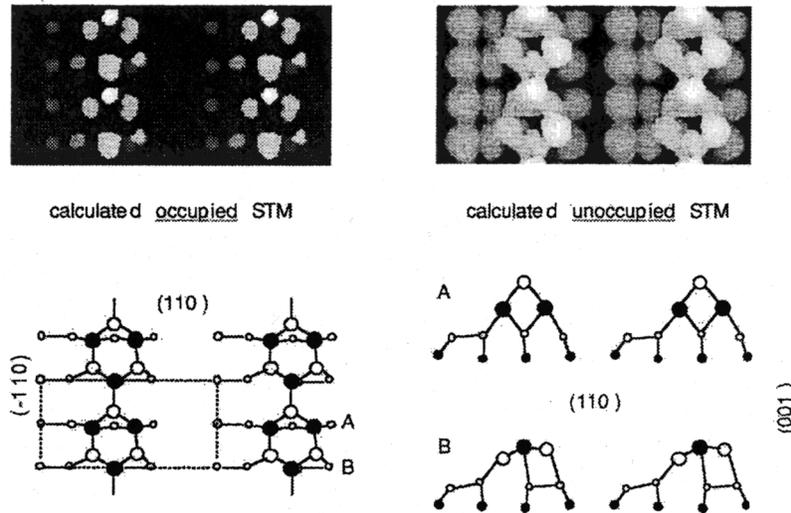


Figure 2. The hexamer reconstruction: Calculated occupied and unoccupied STM image and the atomic structure, where filled (empty) circles are anions (cations).

Also shown in Fig. 2 along with the reconstruction model are calculated STM images for InP. We computed the STM 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 hexamer is not the experimentally observed reconstruction. The top In atom of the hexamer(2×4) reconstruction model has an 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 likely that this hexamer( $2\times 4$ ) 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 hexamer( $2\times 4$ ) reconstruction would follow the general rule.

Let us now consider the mixed dimer( $2\times 4$ ) reconstruction. 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 that will be observed in experiment.

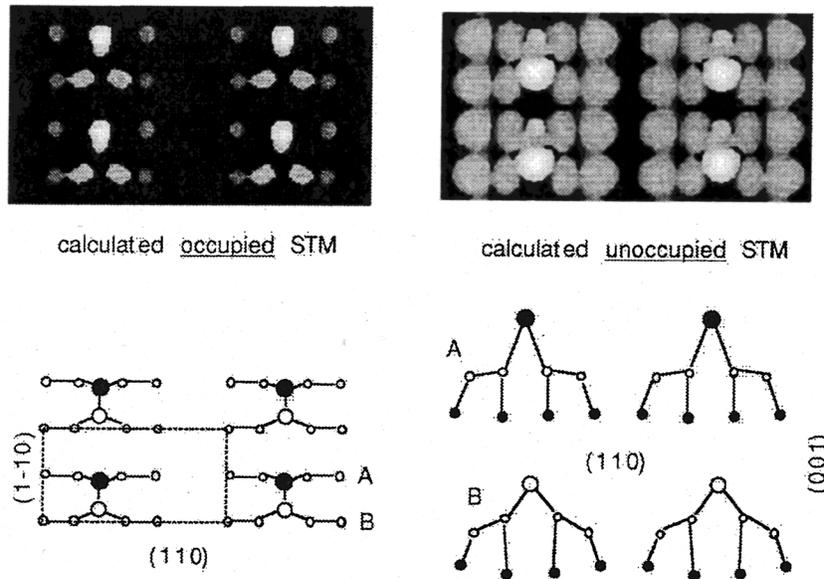


Figure 3. The mixed dimer reconstruction: Calculated occupied and unoccupied STM image and the atomic structure, where filled (empty) circles are anions (cations).

Furthermore, the occupied charge density (Fig. 3) reveals a trimer pattern in excellent agreement with experiment. The trimer pattern consists of the three bright spots, which are repeated with a ( $2\times 4$ ) periodicity. The so-called “head” consists of the occupied dangling bond of the top P atom, the so-called “ears” 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 Å, between head and ear 3.5 Å along the (100) direction, and the height difference between the head and ears amounts to 0.4 Å. Experimentally, besides the trimer pattern, there was an infrequent dimer pattern observed. This is easily explained by replacing the additional top In atom by a P atom. This structure is denoted as  $\alpha 2(2\times 4)$  ( $SPR_{CR}=3$ ) and as seen from Fig. 1 also has 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. 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.

We performed the same analysis for GaAs. In the case of GaAs, we show the surface energy of three cation-rich reconstructions 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 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 we 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. 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  $SRP_{CR}$ . 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:

$$SRP_{AR} = N_a - N_{a-a} + 2N_{c-c}$$

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  $SRP_{AR}$ . Therefore, there are only a few possible anion-rich surface reconstruction patterns with a low  $SRP_{AR}$ .

### 2.3. Journal Articles

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