

## Stress-induced anisotropy of phosphorous islands on gallium arsenide

C. H. Li

*Chemical Engineering Department, University of California–Los Angeles, Los Angeles, California 90095-1592*

L. Li

*Department of Physics and Laboratory for Surface Study, University of Wisconsin, Milwaukee, Wisconsin 53201*

Q. Fu, M. J. Begarney, and R. F. Hicks<sup>a)</sup>

*Chemical Engineering Department, University of California–Los Angeles, Los Angeles, California 90095-1592*

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The initial growth of  $(2\times 4)$  phosphorous islands on  $(4\times 2)$  terraces of gallium arsenide (001) has been studied. The islands grow anisotropically in the  $[110]$  direction with an aspect ratio of approximately 8 to 1 at moderate coverages. The distribution of island widths in the  $[\bar{1}10]$  direction follows a Gaussian function. The mean width increases from  $24\pm 6$  to  $47\pm 11$  Å as the phosphorous coverage increases from 0.10 to 0.85 monolayers. Evidently, the island anisotropy is caused by stress imposed on the underlying gallium layer by the smaller, more tightly bound phosphorous dimers. © 2000 American Institute of Physics. [S0003-6951(00)01640-5]

Metalorganic vapor phase epitaxy (MOVPE) and molecular beam epitaxy have been used extensively for the growth of compound semiconductor heterostructures and superlattices.<sup>1,2</sup> Since the interface smoothness is greatly influenced by the surface morphology during growth, it is important to understand what physical and chemical processes control this property of the material. For example, atomic layer epitaxy and migration enhanced epitaxy have been shown to improve surface morphology.<sup>3,4</sup> In these techniques, the group III and V atoms are alternately supplied to the substrate to enhance the surface mobility of adsorbed species. In order to fabricate a heterojunction or superlattice, one must alternate the composition of the compound semiconductor film, in many cases by switching the group V elements. This can introduce stress into the film. While numerous studies have been made of the nucleation and growth of homoepitaxial films,<sup>5–7</sup> not many have focused on the growth of heterogeneous epitaxial compound semiconductors.<sup>8</sup>

In this article, we present a study of the initial stages of phosphorous island growth on the gallium-rich GaAs (001)- $(4\times 2)$  surface. The group V elements were deposited by decomposing phosphine on the surface in ultrahigh vacuum at temperatures between 310 and 380 °C. Using scanning tunneling microscopy (STM), we found that the phosphorous islands grow primarily in the  $[110]$  direction, with a width varying between 24 and 48 Å in the  $[\bar{1}10]$  direction. To compare this to the homoepitaxy of gallium arsenide, we have studied the formation of arsenic islands on the  $(4\times 2)$  surface via the decomposition of arsine. In this case, the island anisotropy is much less, about 2 to 1. We propose that the phosphorous island growth is restricted in the  $[\bar{1}10]$  di-

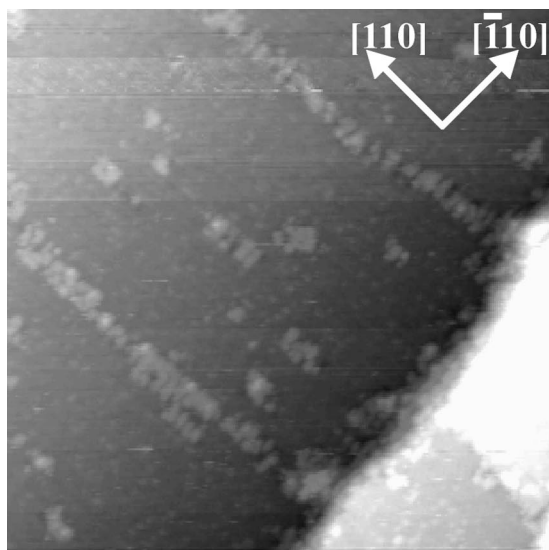
rection, because of a buildup of compressive stress on the gallium sublattice.

The samples were prepared by growing gallium arsenide films, 0.5 μm thick, on GaAs (001) substrates in an MOVPE reactor.<sup>9</sup> After growth, the samples were transferred directly into an ultrahigh vacuum chamber with a base pressure of  $2.0\times 10^{-10}$  Torr. The GaAs (001) crystals were annealed at 793 K for 30 min to obtain a clean and well-ordered gallium-rich  $(4\times 2)/c(8\times 2)$  reconstruction,<sup>9</sup> and this was verified by low-energy electron diffraction and STM.

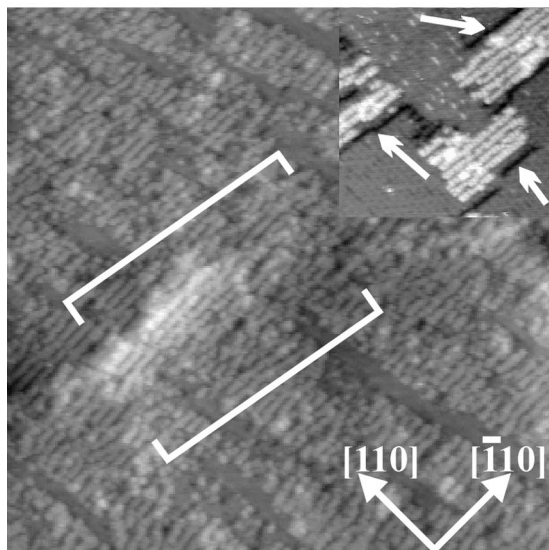
Phosphine and arsine were introduced into the chamber at  $1\times 10^{-5}$  Torr through a leak valve for 20–100 min ( $1.2\text{--}6.0\times 10^4$  L,  $1\text{ L}=10^{-6}$  Torr s). During the adsorption experiments, all the filaments in the chamber were turned off. It was important to do this, otherwise the molecules dissociated on the filament and caused  $\text{PH}_x$ , or  $\text{AsH}_x$ , and H fragments to adsorb onto the surface and yield anomalous results. Scanning tunneling micrographs were obtained after dosing to different coverages at a sample bias from  $-2.0$  to  $-4.0$  V and a tunneling current of 0.5 nA.<sup>9</sup>

Shown in Fig. 1(a) is a filled-states STM image taken after depositing 0.10 monolayers (ML) of phosphorous at 310 °C. The phosphorous generates islands that exhibit a  $(2\times 4)$  reconstruction. The  $(2\times 4)$  is distinguished by light gray rows that extend for a short distance in the  $[\bar{1}10]$  direction and repeat every 16 Å in the  $[110]$  direction. The gray intensity is associated with the filled lone pairs of electrons in the dangling bonds of the phosphorous dimers. Examination of the STM image reveals that some of the  $(2\times 4)$  islands extend for long distances parallel to the  $[110]$  axis. By contrast their average width is  $\sim 25$  Å. The aspect ratio is about 30 to 1 for the islands seen in Fig. 1(a). Inspection of many different surfaces with coverages ranging from 0.1 to 0.5 ML yields an average aspect ratio of 8 to 1 for the P-rich  $(2\times 4)$  islands.

<sup>a)</sup>Author to whom correspondence should be addressed; electronic mail: rhicks@ucla.edu



(a)



(b)

FIG. 1. Scanning tunneling micrographs of the phosphorous-rich ( $2\times 4$ ) islands on GaAs (001)-( $4\times 2$ ) surfaces: (a)  $\theta_p=0.10$  ML and  $T_{\text{dep}}=310$  °C; (b)  $\theta_p=0.85$  ML and  $T_{\text{dep}}=380$  °C; and inset  $\theta_p=0.25$  ML and  $T_{\text{dep}}=380$  °C. The image areas are (a)  $1160\times 1160$  Å<sup>2</sup>, (b)  $1300\times 1300$  Å<sup>2</sup>, and inset  $420\times 420$  Å<sup>2</sup>.

In Fig. 1(b), we present a filled-states STM image of the GaAs (001) surface after depositing 0.85 ML of phosphorous at 380 °C. Here, the surface is covered by a series of narrow ( $2\times 4$ ) islands separated by slender gaps 20–40 Å across. The islands are for the most part continuous in the [110] direction. Notice that the gaps disappear near the step edges, so that this region is nearly completely covered by the ( $2\times 4$ ) reconstruction (see bracketed region). The same experiments described above were repeated for arsenic deposition on the GaAs ( $4\times 2$ ) surface at 380 °C. In this case, the As-rich ( $2\times 4$ ) islands exhibit much less anisotropy, and randomly cover the surface. An aspect ratio of about 2 to 1 is observed at As coverages from 0.05 to 0.65 ML.

Shown in the insert of Fig. 1(b) is a small scale STM image of ( $2\times 4$ ) islands on the ( $4\times 2$ ) at a phosphorous coverage of 0.25. Vacancy lines appear along the edges of the

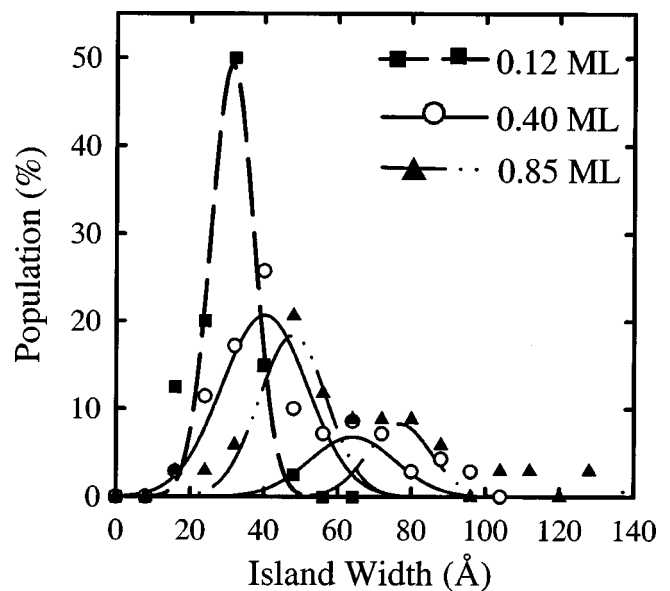


FIG. 2. The probability distribution of the island width in the  $[\bar{1}10]$  direction at 380 °C.

islands, as indicated by the white arrows. The lines are approximately one monolayer deep (1.3 Å), and are found adjacent to both the As-rich and P-rich ( $2\times 4$ ) islands. These results indicate that gallium atoms have diffused out of the ( $4\times 2$ ) surface. This is not surprising, because the Ga coverage on a ( $4\times 2$ ) surface is 0.75 ML.<sup>10</sup> However, for the group V-rich islands to grow on top of the Ga-rich surface, an additional  $\frac{1}{4}$ – $\frac{1}{2}$  ML of Ga is required for the nucleation of the  $\beta 2(2\times 4)$  or  $\alpha(2\times 4)$  phases, respectively.<sup>11</sup> It is observed that the step edges quickly saturate with ( $2\times 4$ ) islands upon deposition of phosphorous or arsenic. Evidently, the step edges are a ready source of gallium atoms for building ( $2\times 4$ ) islands.

Presented in Fig. 2 are distributions of the width of the ( $2\times 4$ ) islands as a function of phosphorous coverage, after dosing  $\text{PH}_3$  at 380 °C. The plots were constructed by mea-

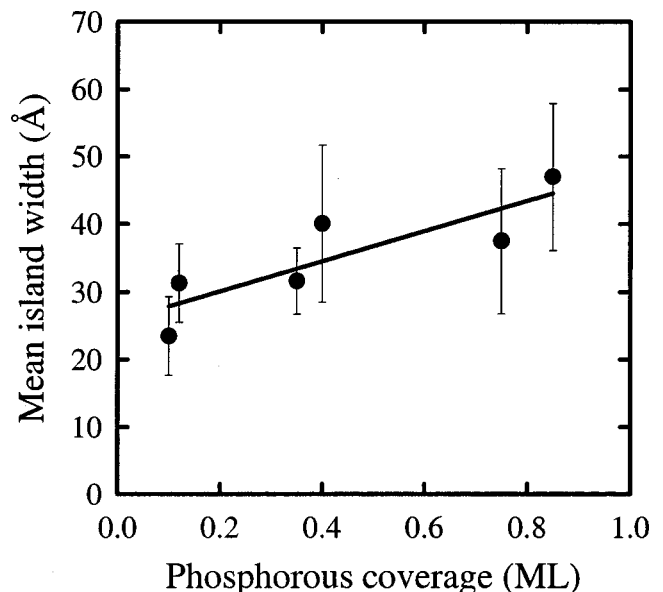


FIG. 3. Mean island width as a function of coverage.

TABLE I. Comparison of the bonding properties of adsorbed phosphorous, arsenic, and antimony dimers on GaAs (001)-(4×2).

	Ref.	P-P	As-As	Sb-Sb
Covalent radii (Å)	16	1.28	1.39	1.59
Dimer bond length (Å)	17,18	2.23 (on InP)	2.50 (on GaAs)	2.86 (on Sb-GaAs)
Dimer bond strength (kcal/mol)	16	490	382	299
Ga back bond strength (kcal/mol)	16	230 (GaP)	210 (GaAs)	209 (GaSb)
Second layer Ga-Ga distance (Å) (in $[\bar{1}10]$ direction)	17-19	...	3.58 (on GaAs)	3.73 (on Sb-GaAs)

asuring the widths of over 400 islands in a series of STM images corresponding to each coverage. The experimental results are shown as data points, and the dashed, solid, and dashed-dotted lines are Gaussian fits of the data with the function

$$y = \frac{A}{\sigma\sqrt{2\pi}} \exp -0.5 \left( \frac{x-x_c}{\sigma} \right)^2,$$

where  $x_c$  is the mean,  $\sigma$  is the variance, and  $A$  is the total area under the curve.

At 0.12 ML of phosphorous, the distribution exhibits a sharp peak at  $31 \pm 6$  Å. We notice that the island widths at higher coverages (i.e., >0.40 ML) have a bimodal distribution, and therefore, have been fitted with two Gaussian curves. At 0.40 ML of phosphorous, the island widths for the two distributions are 40 and  $64 \pm 12$  Å. These values increase to 47 and  $76 \pm 12$  Å at 0.85 ML of phosphorous. The same Gaussian distribution is observed for islands grown at 310 °C, with the mean width increasing from  $24 \pm 6$  Å at  $\theta_p=0.10$  ML, to 37 and  $56 \pm 11$  Å at  $\theta_p=0.75$  ML. We are not certain why a bimodal distribution is observed at higher coverages, a likely explanation would be island coalescence. At higher dosages, small islands may nucleate and grow in the gaps between the larger islands. These small structures may be unstable and incorporate into the larger ones by a process similar to Ostwald ripening.

In Fig. 3, the mean island width is plotted against the phosphorous coverage following  $\text{PH}_3$  decomposition at 310 and 380 °C. In cases where a bimodal distribution is recorded, only the peaks at the lower values have been included in the plot. The data points fall onto a straight line, indicating that the island width depends only on coverage and is relatively insensitive to temperature. In addition, the widths vary over a narrow range from about 30 to 45 Å.

We propose that island growth in the  $[\bar{1}10]$  direction is restricted by stress imposed by the phosphorous dimers on the second-layer gallium atoms. It is well known that dimerization strains the surface by pulling together the atoms underneath the dimers.<sup>12-15</sup> On Si (100), this strain is relieved by forming alternating domains of (2×1) and (1×2) reconstructions, and by generating dimer vacancies.<sup>13</sup> In the case of germanium deposition on Si (100), a well-ordered

(2×N) structure is formed with equally spaced vacancy lines perpendicular to the dimer bonds.<sup>15</sup> Here, the vacancy lines relieve the stress on the underlying layer.

In our case, a different interface is formed depending on whether phosphorous or arsenic is deposited on the gallium-rich GaAs (001) surface. In Table I, we compare the stress at the interface for three group V elements: P, As, and Sb. The phosphorous atoms exhibit the shortest dimer bond length and the strongest backbonds to gallium.<sup>16-19</sup> Consequently, the phosphorous displaces the second-layer Ga atoms the most from their bulk positions, which is 4 Å apart. Since the stress builds up as each additional P dimer is attached in the  $[\bar{1}10]$  direction, a critical value will be reached where the strain energy prevents further growth. On the other hand, since the As and Sb dimers impose less stress on the subsurface gallium atoms, they produce (2×4) islands with much lower anisotropy.<sup>20</sup> It should be noted that the phosphorous-rich (2×4) islands can extend long distances along the [110] crystal axis, because the stress in this direction is relieved by dimer vacancies and trenches.

These results highlight the role that stress plays in the heteroepitaxy of compound semiconductor thin films. A better understanding of this phenomenon could lead to new methods of generating nanostructures by MOVPE.

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