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# An STM Survey of As/Ge(mnn) and P/Ge(mnn) Surfaces

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## ABSTRACT

This paper contains a few representative results of a scanning tunneling microscope (STM) survey of Ge surfaces after exposure to arsenic and phosphorous.  $\text{PH}_3$  (phosphine)- and  $\text{As}_4$ -exposed surfaces remain flat, whereas  $\text{AsH}_3$  (arsine)-exposed surfaces can become nano-facetted due to etching. Some examples are given, and more general trends are discussed.

## 1. Introduction

Currently, high-efficiency GaAs/GaN tandem cells are grown on Ge substrates. However, little is known about the nucleation of the initial layers on the Ge surface. One complication is that the initial nucleation surface is not clean Ge, but either arsenic- or phosphorous-exposed Ge. For this reason, we have conducted a study of the effect of arsenic and phosphorous exposure on Ge surfaces. In order to understand a range of technologically-relevant miscut directions, we have studied Ge(mnn) surfaces between (100) and (111).

## 2. Experimental Details

All surfaces were prepared in a metal-organic chemical vapor deposition (MOCVD) chamber under 50–70 torr of  $\text{H}_2$  carrier gas flowing at 6–8 L/min. The group V source was either  $\text{PH}_3$ ,  $\text{AsH}_3$  or background  $\text{As}_4$ .

After preparation in the MOCVD chamber, samples were quenched to room temperature and transferred under vacuum to an ultra-high vacuum (UHV) chamber for study with low-energy electron diffraction (LEED), Auger electron spectroscopy (AES) and scanning tunneling microscopy (STM). All surfaces were studied as-quenched, with no additional surface preparation after leaving the MOCVD chamber.

## 3. Definitions

In this paper, the index (mnn) is limited to surfaces between (100) and (111), in other words,  $m > n$ . Figure 1 shows the relative orientations of the crystal surfaces to be discussed in this paper.

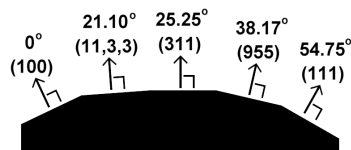


Figure 1. Schematic diagram of the facets discussed in this paper, with angles referenced to (100).

As/Ge refers to an arsenic-exposed Ge surface, while P/Ge refers to a phosphorous-exposed Ge surface, regardless of the source of arsenic or phosphorous. To specify the exact source of arsenic or phosphorous, a slightly different nomenclature is used.  $\text{PH}_3$ :Ge,  $\text{AsH}_3$ :Ge and  $\text{As}_4$ :Ge denote a Ge surface which has been exposed to (respectively) phosphine, arsine and elemental arsenic. In this paper the  $\text{As}_4$ :Ge surfaces were prepared by exposure to the background  $\text{As}_4$  in our MOCVD chamber.

## 4. Results

We have found that  $\text{PH}_3$ :Ge(mnn) and  $\text{As}_4$ :Ge(mnn) surfaces remain flat for the conditions we have studied, while  $\text{AsH}_3$ :Ge(mnn) surfaces can be either flat or nano-facetted, depending upon the exact sample-preparation conditions. Here we will provide three specific examples, then discuss general trends.

### 4(a). $\text{PH}_3$ :Ge(311)

Figure 2 is an STM image of  $\text{PH}_3$ :Ge(311). It is very flat, and has adopted an  $n \times 2$  reconstruction. The "2" refers to the width of the obvious rows, which have a spacing of 13.3 Å, while the "n" refers to the regularly-spaced breaks along each row. LEED analysis indicates that these breaks occur every 6 to 7 atoms ( $n = 6$  or 7). In the literature, similar gaps in surface reconstructions have been attributed to strain relief [1–4].

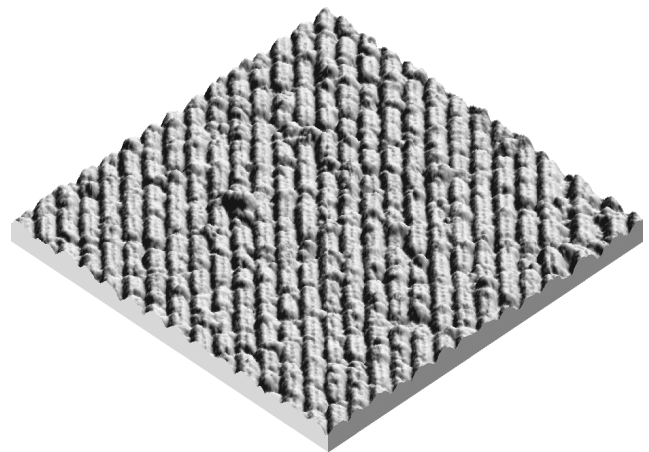


Figure 2. P/Ge(311) prepared by annealing a Ge(311) surface in an MOCVD chamber under 1.2 torr  $\text{PH}_3$  at 570°C for 5 min.

Image size: 400 Å × 400 Å.

#### 4(b). As<sub>4</sub>:Ge(311)

Figure 3 is an STM image of As<sub>4</sub>:Ge(311). This surface was prepared by annealing a Ge(311) surface in an MOCVD chamber under H<sub>2</sub> and background As<sub>4</sub>. It also remains flat, but with a 2×3 reconstruction. The "3" indicates that the row spacing is 19.9 Å. Note that this is different from the row spacing seen for PH<sub>3</sub>:Ge(311). The "2" indicates that a subtle two atom periodicity along the rows is observed with LEED.

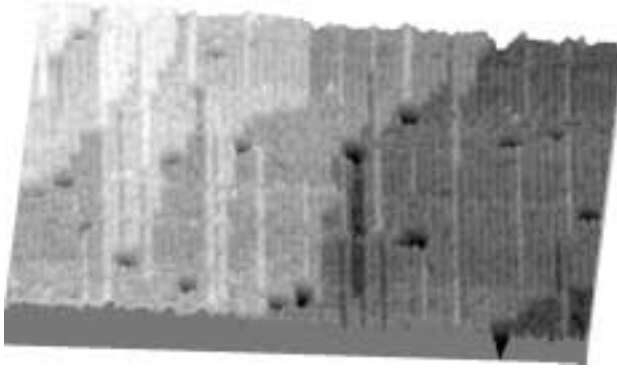


Figure 3. As/Ge(311) prepared by annealing a Ge(311) surface in an MOCVD chamber under background As<sub>4</sub> for 50 min. while slowly lowering the temperature from 640° to 470°C. Some steps are observed, due to a slight unintentional misorientation of the substrate away from (311).

Image size: 2000 Å × 2000 Å.

#### 4(c). AsH<sub>3</sub>:Ge(311)

Figure 4 is an STM image of AsH<sub>3</sub>:Ge(311). In contrast to the previous two examples, this surface is nano-faceted. This nano-facetting is a result of AsH<sub>3</sub>-etching of the surface. (No etching of Ge is observed for either PH<sub>3</sub> or As<sub>4</sub>.) Two preferred faceting directions are observed: (11,3,3) and (955).

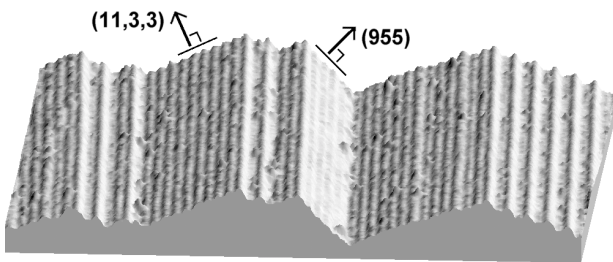


Figure 4. As/Ge(311) formed by annealing a Ge(311) surface under 1.2 torr AsH<sub>3</sub> for 30 min. at 640°C. An (11,3,3) and a (955) facet have been labelled. The rightmost facet can be formed by interlacing (11,3,3) and (955) surface unit cells.

Image size: 1500 Å × 1500 Å.

#### 5. Discussion

The preceding (311) examples serve as a basis for discussing the entire range of As/Ge and P/Ge (mnn) surfaces. Similar results have been obtained for Ge(211), Ge(311), Ge(411), Ge(511), and vicinal Ge(100) [5, 6] miscut 2, 6 and 9° toward (111).

For the conditions we have studied, PH<sub>3</sub>:Ge(mnn) surfaces always remain flat. This suggests an energetic driving force, such as surface tension, which tends to make the surfaces flat.

As<sub>4</sub>:Ge(mnn) surfaces also remain flat for the conditions we have studied. Moreover, it is possible to flatten a previously nano-faceted Ge(mnn) surface by heating it under As<sub>4</sub>. This indicates that subsurface Ge can rise to the surface and travel great distances before relocating in a more desirable location.

Because AsH<sub>3</sub> etches Ge, the AsH<sub>3</sub>:Ge(mnn) surfaces are more complicated. As with the As<sub>4</sub> case, thermal energy still causes subsurface Ge to rise to the surface. However, the etching process removes some fraction of this Ge before it has a chance to relocate. If all of the Ge is removed, and none relocates, the resulting surface can become completely faceted. If most of the Ge relocates (compared to the etching rate), the resulting surface will be flat. The As<sub>4</sub> case represents one extreme in which all of the Ge relocates (none is etched).

This balance between the supply, removal, and relocation of Ge during AsH<sub>3</sub> etching is consistent with our observations, but more work needs to be performed before it is understood in detail. Nonetheless, we are now able to describe the general trends, and have identified three principle nano-facetting directions: (100), (11,3,3) and (955).

#### 6. Conclusions

The effects of arsenic and phosphorous exposure on Ge(mnn) substrates has been studied. We find that As<sub>4</sub>- and PH<sub>3</sub>-exposed Ge surfaces remain flat, whereas AsH<sub>3</sub> exposure can induce nano-facetting. This behavior was observed for a range of Ge(mnn) surfaces between (100) to (111).

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