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A Scanning Tunneling Microscopy Study of As/Ge(mnn) and P/Ge(mnn) Surfaces

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Abstract: Ge(mnn) surfaces between (100) and (111) were annealed under either arsine or phosphine in a metal-organic chemical vapor deposition chamber, then imaged with a scanning tunneling microscope. In general, arsine-exposed Ge surfaces are facetted, while phosphine-exposed surfaces remain flat. For the arsine-exposed Ge surfaces, four stable facetting directions have been identified: (100), (11,3,3), (955), and (111).

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1. Introduction

To better understand the nucleation of GaAs and $GaInP_2$ on Ge, we have performed a survey of Ge surfaces after exposure to either arsine (AsH_3) or phosphine (PH_3) in a metal-organic chemical vapor deposition (MOCVD) chamber. Vicinal surfaces with miscut angles between (100) and (111) were studied.

Our results for AsH_3 exposure are quite different than for PH_3 exposure. Most significantly, we find that AsH_3 etches Ge, whereas PH_3 does not [1]. In addition, AsH_3-exposed Ge surfaces tend to facet. PH_3-exposed surfaces remain flat, independent of the miscut angle.

The facetting of As/Ge surfaces has proven to be quite interesting, and will be the focus of most of this paper. For miscut orientations near (100) and (111), we find (100) and (111) terraces [1,2], in complete agreement with previously published results [3-8]. Prior to this study, little was known about the higher-angle miscuts, however. For this reason, models for nucleation on high-angle vicinal As/Ge surfaces are based on bulk-like low-index surfaces such as (211).

In sharp contrast, our results show that low-index As/Ge surfaces such as (211), (311), (411), and (511) are neither bulk-like, nor are they stable under AsH_3 exposure. Instead, we find that the stable As/Ge surfaces are (100), (11,3,3), (955), and (111). Furthermore, the (11,3,3) and (955) As/Ge surfaces are heavily reconstructed.

2. Experimental Details

All surfaces were prepared in an MOCVD chamber under 50–70 torr of H_2 carrier gas flowing at 6–8 L/min. The group V source was either arsine (AsH_3), phosphine (PH_3), or background 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 planes of the $[0\bar{1}1]$ zone with m>n. As shown in Figure 1, this spans a range of miscut orientations from (100) to (111).

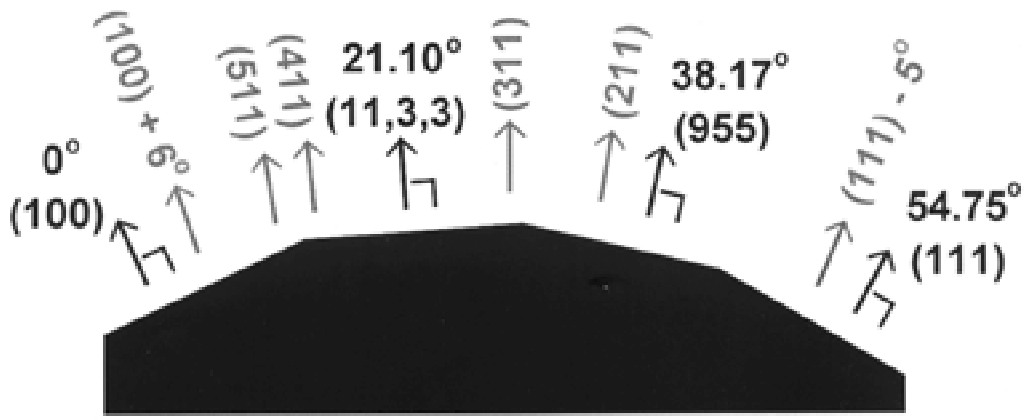

Figure 1: A diagram showing the relative orientations of the various surfaces discussed in this paper.

As/Ge refers to an arsenic-exposed Ge surface, whereas 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. A Ge surface that has been exposed to arsine will be referred to as an AsH_3:Ge surface. Similarly, a PH_3:Ge surface is a Ge surface that has been exposed to phosphine.

The terms "stable" and "unstable" will have very specific meanings in this paper. A "stable" surface cannot be facetted by AsH_3 exposure. In contrast, "unstable" As/Ge surfaces can either facet or remain flat, depending on the exact AsH_3 exposure conditions.

4. Results

(a) Stable AsH_3:Ge(mnn) Surfaces

Under AsH_3 etching, As/Ge(100), (11,3,3), (955), and (111) surfaces are all stable.

Our results for As/Ge(100) and (111) are consistent with earlier studies. The AsH_3:Ge(100) surface consists of a simple 2×1 reconstruction in which As dimers terminate the bulk Ge lattice [1,2], as has been observed previously for tertiarybutylarsine-exposed Ge in an MOCVD environment [3] and for As_2- and As_4-exposed Ge in a UHV environment [4-6].

As/Ge(111) surfaces formed by As_4 exposure under UHV consist of a simple 1 × 1 reconstruction in which As atoms terminate the Ge bulk lattice [7-9]. Each As atom is bonded to three Ge atoms, leaving a lone electron pair protruding away from the surface. Although this bonding configuration is very desirable chemically, it places the surface As atoms under tension [10]. It has been shown that this strain produces a network of three-atom-wide trenches [7,8]. The AsH_3:Ge(111) surfaces we have observed are quite similar and contain all of the same basic features. The only difference is that the trench networks appear to be more hexagonal and more closely spaced for the conditions we have studied.

In contrast to the relatively minor reconstructions and relaxations of the As/Ge(100) and (111) surfaces, the As/Ge(11,3,3) and (955) surfaces are heavily reconstructed. As seen in Figure 2, the As/Ge(11,3,3) surface consists of parallel ridges spaced 23.6 Å apart, consistent with the observed 1 × 1 LEED pattern. This image shows the strong tendency toward (11,3,3). Only (11,3,3) terraces separated by steps are observed.

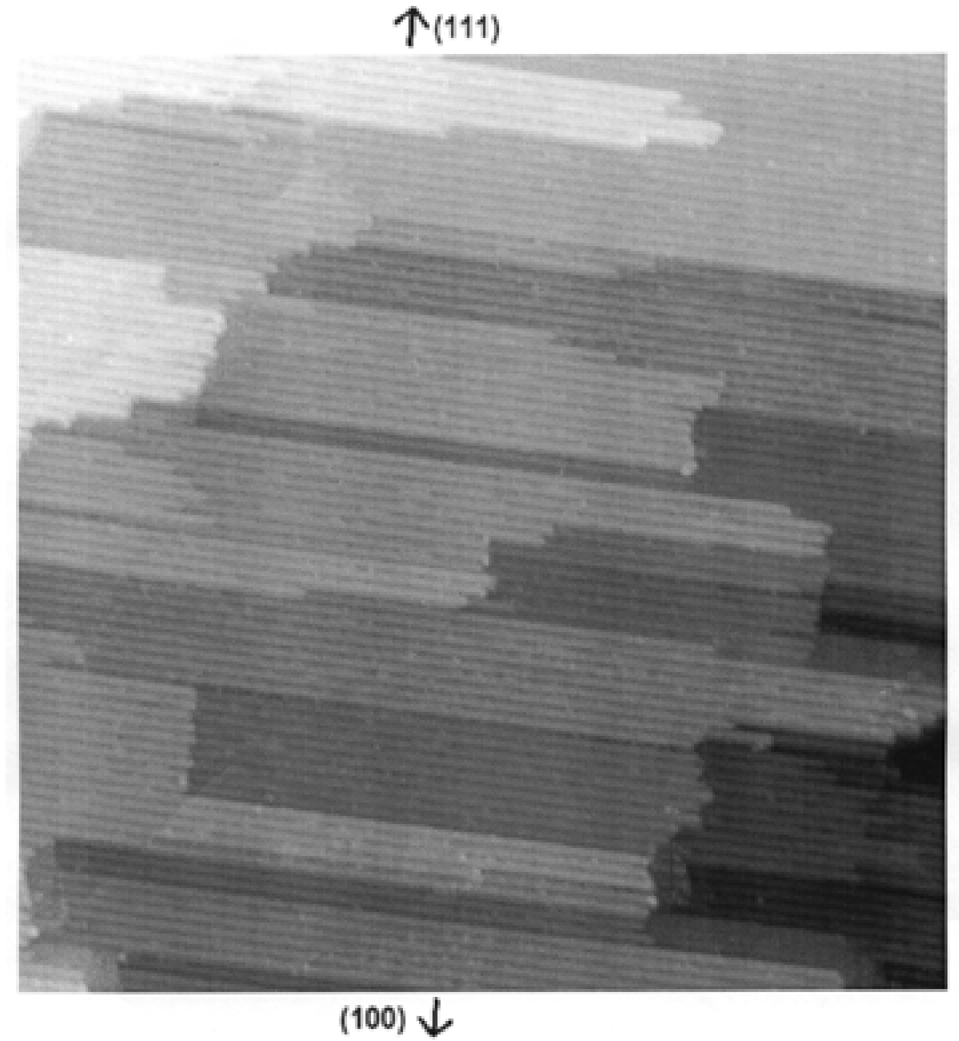

Figure 2: A 2000 Å × 2000 Å image of AsH_3:Ge(11,3,3) annealed under 1.2 torr AsH_3 at 560°C for 20 minutes, then cooled to room temperature under AsH_3. V_{sample} = -2.0 V and I_{tun} = 0.1 nA.

At slightly higher resolution (Figure 3), several different structural motifs become visible. The principal structures are the regularly spaced parallel ridges. These ridges appear to be very closely related to the double-row steps seen on vicinal As/Ge(100) surfaces [1]. Between each pair of ridges there is a gap. The simplest way to span these gaps appears to be with short sections of (311)-oriented surface. An example is labeled with a "1" in Figure 3. In some locations this gap region has been etched ("2" in Figure 3). In other locations a ridge has formed where a gap ought to be ("3" in Figure 3).

Although the atomic structure of these various motifs is unknown, a definite hierarchy exists. The ridges are the most stable structure on the surface. This is evident in Figure 3, where the gaps between ridges are being preferentially etched while the ridges remain intact.

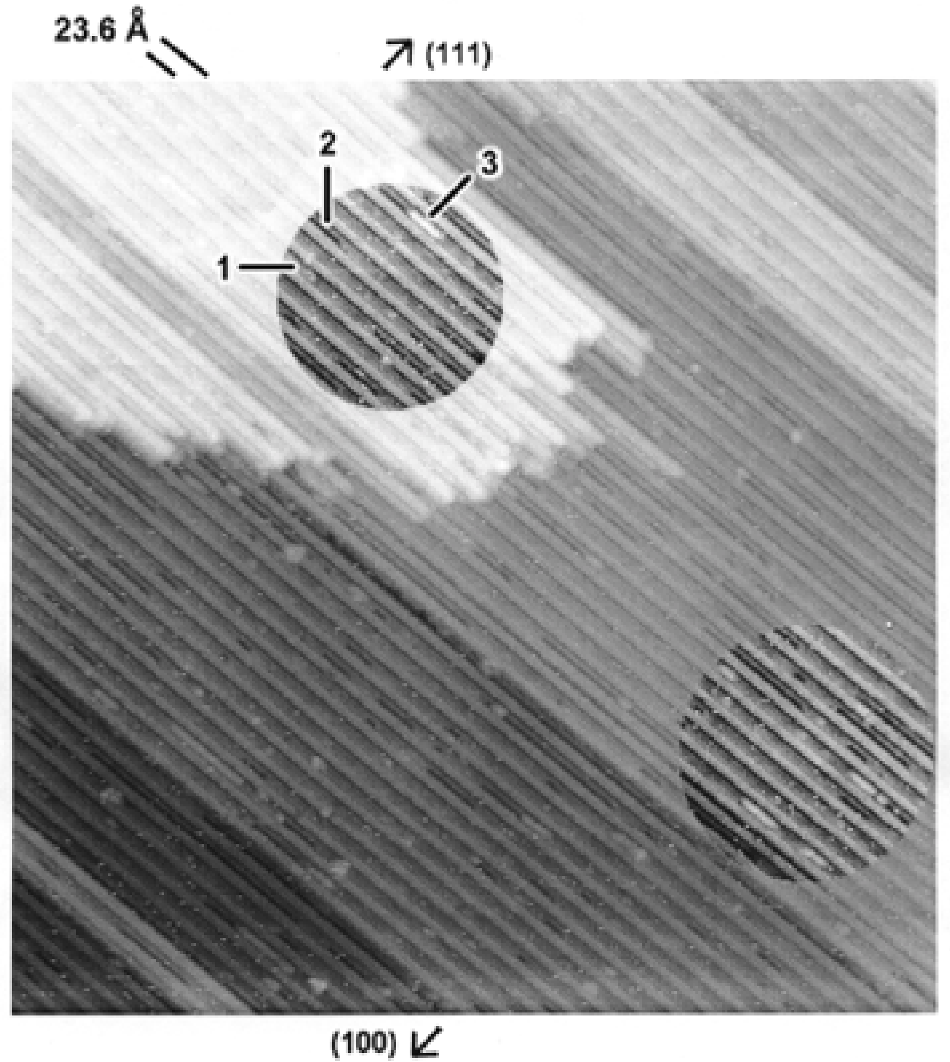

Figure 3: A higher-resolution 1000 Å × 1000 Å image of the AsH_3:Ge(11,3,3) surface shown in Figure 2. In the two circled regions, the gray scale has been expanded to reveal surface details. An explanation of features "1," "2," and "3" can be found in the text. V_{sample} = -2.0 V and I_{tun} = 0.1 nA.

The final stable surface to be identified in this study is As/Ge(955). Figure 4 shows that the As/Ge(955) surface consists of ridges spaced 22.9 Å apart, consistent with the observed 1 × 1 LEED pattern. Although it is possible that these (955) ridges are structurally similar to (11,3,3) ridges, their behavior seems quite different.

In particular, it is possible to travel from one (955) terrace to another via a ramp (an example is labeled with an "r" in Figure 4). These ramps are actually "nano-facets" facing toward nearby directions [such as (211) or (533), for example]. These nano-facets are significant. Notice that similar facets do not exist on the As/Ge(11,3,3) surfaces shown in Figures 2 and 3. This indicates that As/Ge(11,3,3) is much more stable than any nearby facetting direction, whereas As/Ge(955) is not.

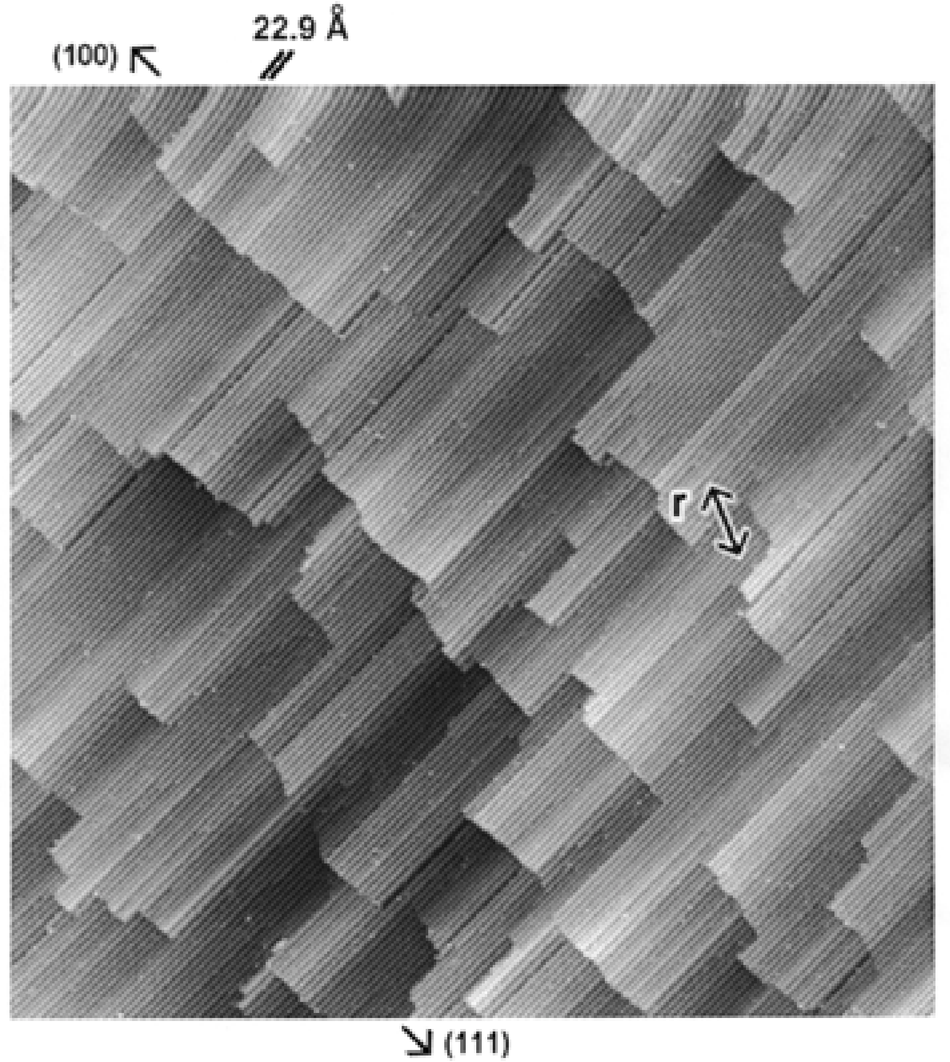

Figure 4: A 3500 Å × 3500 Å image of AsH_3:Ge(955) annealed under 1.2 torr AsH_3 at 560°C for 20 minutes, then cooled to room temperature under AsH_3. A "ramp" between two adjacent (955) terraces has been labeled with an "r" (see text). V_{sample} = -2.0 V and I_{tun} = 0.08 nA.

(b) Unstable AsH_3:Ge(mnn) Surfaces

We have studied the effect of AsH_3 exposure on many other miscut directions: (511), (411), (311), (211), (100) miscut 2°, 6°, and 9° toward (111), and (111) miscut 5° toward (100). In each case it is possible to find AsH_3 exposure conditions that induce facetting. The degree of facetting seems to depend on many factors, such as miscut angle, annealing time, annealing temperature, AsH_3 partial pressure, and background As_4 partial pressure. Although the interaction of these factors can become quite complicated, some general trends have emerged.

First of all, when these unstable surfaces facet, they tend to facet toward the stable directions. For example, surfaces miscut within a few degrees of (11,3,3) tend to become vicinal (11,3,3) surfaces, consisting solely of (11,3,3) terraces separated by steps. Similarly, near (100) and (111), there is a tendency toward (100) and (111) facetting, respectively. As noted earlier, the tendency to form (955) facets is not as strong.

Away from these stable directions, the facetting is generally incomplete. As an example, in Figure 5 we show an As/Ge(511) surface that is only partially facetted toward (100) and (11,3,3). In addition to these two stable facetting directions, there are obvious (511) regions and a variety of less obvious intermediate facets.

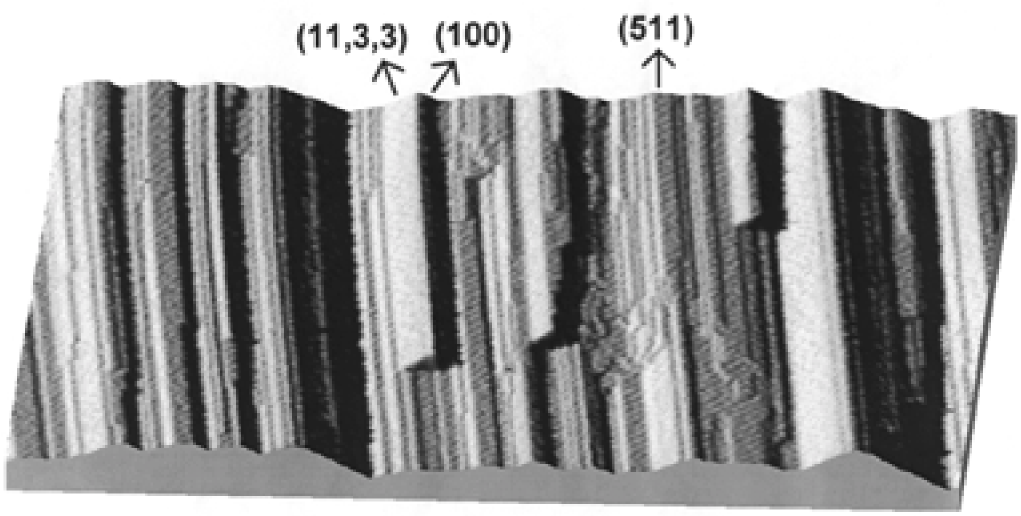

Figure 5: A 1.0 µm × 1.0 µm image of AsH_3:Ge(511) annealed under 1.2 torr AsH_3 at 640°C for 30 minutes, then cooled to 300°C under AsH_3, then cooled to room temperature under H_2. This image has been artificially illuminated from the left. The surface has partially facetted toward (11,3,3) and (100), as labeled. V_{sample} = -2.0 V and I_{tun} = 0.03 nA.

Finally, it is important to note that it is possible to expose an unstable surface to AsH_3 without inducing facetting. The most obvious method is to keep the AsH_3-etching to a minimum by reducing the temperature, AsH_3 partial pressure, and total AsH_3 exposure time. Taken to an extreme, background As_4 can be used as the sole arsenic source. Under As_4 exposure, we observe neither etching nor facetting of the resulting As/Ge surfaces.

A second, much more effective method is to increase the temperature and reduce the AsH_3 partial pressure. This method relies on thermal annealing to flatten the surface. Using this method we have been able to completely flatten even very heavily facetted surfaces.

To give two examples, we have been able to use these methods to obtain very flat vicinal (100) and (111) surfaces. Flat vicinal (100) consists of (100) terraces separated by regularly spaced, four-monolayer (5.67 Å high) steps. Similarly, flat vicinal (111) consists of (111) terraces separated by regularly spaced steps with a height of 6.53 Å (two bilayers). This is different from *facetted* vicinal (100) or (111), which consist of large (100) or (111) facets separated by bunched steps and/or other facets.

(c) PH_3:Ge(mnn) Results

In contrast to AsH_3, etching of Ge by PH_3 is negligible. Perhaps for this reason, the morphology of PH_3:Ge(mnn) surfaces is much simpler. They remain flat under all of the conditions we have studied. So far we have studied PH_3:Ge(mnn) for (211), (311), (411), (511), and (100) miscut 2°, 6°, and 9° toward (111) under a variety of annealing conditions, and no significant facetting has been observed.

5. AsH_3:Ge(mnn) Discussion

Throughout this paper, we have been referring to surfaces as "stable" and "unstable." It is important to note that in this paper, a "stable" surface is not necessarily a low energy surface. Since AsH_3 etches Ge, there is a net flow of Ge atoms away from the surface, so the surface is not being held at equilibrium. Therefore, the resulting surface is not necessarily a low energy surface. There could be a kinetic barrier preventing the surface from settling into its lowest energy configuration.

Nonetheless, regardless of the exact reason, it is clear that facetting of the unstable As/Ge surfaces is related to AsH_3 exposure and, unavoidably, to the observed etching. It is also known that thermal annealing can completely flatten even the most heavily facetted surfaces. The degree of facetting is therefore the result of a competition between AsH_3-induced facetting and flattening of these facets by annealing. Although the AsH_3 exposure conditions can be carefully controlled so as to completely flatten or completely facet a surface, most of the surfaces we have observed are in more complicated, partially facetted configurations.

The PH_3-exposed surfaces provide a nice counterexample in that no facetting or etching has been observed. Instead, we observe very flat, heavily reconstructed surfaces.

6. Summary

In this paper we have studied the effects of AsH_3 and PH_3 exposure on Ge(mnn) substrates between (100) and (111). We find that four surface orientations are stable and remain flat under AsH_3 exposure: (100), (11,3,3), (955), and (111). We find that Ge(mnn) surfaces in between these principal directions are unstable under AsH_3 exposure. Depending on the exact AsH_3 exposure conditions, these unstable surfaces can either facet or remain flat. Under PH_3 exposure, no facetting has been observed. For a wide variety of annealing conditions, every miscut direction we have studied has remained flat under PH_3 exposure.

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