

12-22-1994

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Recommended Citation

Nogami, J.; Yoshikawa, S.; Glueckstein, J. C.; and Pianetta, P. (1994) "Boron Reconstructed Si(111) Surfaces Produced by B2O3 Decomposition," *Scanning Microscopy*: Vol. 8 : No. 4 , Article 9. Available at: <https://digitalcommons.usu.edu/microscopy/vol8/iss4/9>

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BORON RECONSTRUCTED Si(111) SURFACES PRODUCED BY B₂O₃ DECOMPOSITION

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(Received for publication May 16, 1994 and in revised form December 22, 1994)

Abstract

Scanning tunneling microscopy has been used to study the growth of boron on the Si(111) surface. Boron was deposited in the form of B₂O₃ which was decomposed by heating the substrate. With this technique, it is possible to control the B coverage, and also to produce the well known $\sqrt{3} \times \sqrt{3}$ reconstruction at annealing temperatures as low as 600°C. The optimal conditions for the formation of the $\sqrt{3} \times \sqrt{3}$ surface by B₂O₃ decomposition are given. In addition, the nature of the $\sqrt{3} \times \sqrt{3}$ surface over a range of B coverages and annealing temperatures is described.

Key Words: Scanning tunneling microscopy, boron, silicon, Si(111), B₂O₃.

Introduction

The behavior of Boron on the Si(111) surface has been the subject of intense study within the last several years. Boron induces a $\sqrt{3} \times \sqrt{3}$ reconstruction, and most of the work in this system has focused on this particular ordered phase (Hirayama *et al.*, 1988; Korobtsov *et al.*, 1988). In 1989, several groups proposed a structure for this reconstruction in which the B occupied a three fold site underneath a Si adatom (Bedrossian *et al.*, 1989; Headrick *et al.*, 1989; Lyo *et al.*, 1989). Experimental and theoretical support for this model has followed from many authors (Grehk *et al.*, 1992; Huang *et al.*, 1990; McLean *et al.*, 1990). There are no reports of other ordered phases in the B/Si(111) system.

In most of the prior experimental work, the B reconstructed surface was prepared by heating heavily B doped Si(111) wafers to temperatures in excess of 900°C in order to segregate the dopant to the surface. This segregation process has been studied in detail by surface techniques such as Auger electron spectroscopy, but there is some difficulty in quantifying the B coverage at the surface (Hirayama *et al.*, 1988; Korobtsov *et al.*, 1988; Thibaudau *et al.*, 1989). The nominal density of B in the $\sqrt{3} \times \sqrt{3}$ (hereafter $\sqrt{3}$) phase is 1/3 monolayer (ML), and the segregated dopant concentration is usually assumed to saturate at this value. Scanning tunneling microscope (STM) images have demonstrated that it is possible to produce a largely defect free $\sqrt{3}$ surface by this method (Bedrossian *et al.*, 1989; Thibaudau *et al.*, 1989).

Other studies have deposited B on the surface by sputtering, or exposing the surface to HBO₂, B₁₀H₁₄ or B₂O₃ (Bedrossian *et al.*, 1989; Cao *et al.*, 1993; Hirayama *et al.*, 1988; Lyo *et al.*, 1989). After deposition, the surface is annealed to reconstruct the surface, and also to drive excess B and other species from the surface. For several of these methods, it has been possible to prepare surfaces at below the saturation coverage, or at temperatures below what is necessary to produce the $\sqrt{3}$ phase by dopant segregation. In some of these cases, there is evidence of disorder and possibly

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different bonding sites for the B (Cao *et al.*, 1993; Lyo *et al.*, 1989). The advantage of B deposition over B segregation is the flexibility in preparing surfaces that are not necessarily ideal, single phase $\sqrt{3}$, and moreover, the ability to study the behavior of B on Si(111) over a range of coverages and temperatures.

In this work, B deposited Si(111) surfaces were prepared over a range of annealing temperatures and B coverages by thermal decomposition of B₂O₃. The optimal conditions for the preparation of a defect free $\sqrt{3}$ surface with this method are given. Differences in the surface prepared well away from the ideal conditions are also described.

Methods

Si(111) samples were cut from wafer stock, solvent cleaned and then exposed to ozone producing UV light before being loaded into ultra-high vacuum (UHV) (Tabe, 1984). The samples were flashed above 1150°C to produce a clean, well-ordered 7×7 surface as seen by low energy electron diffraction (LEED) and STM. B₂O₃ was sublimed from crystals heated in W wire baskets. Evaporation rates were measured by a quartz crystal microbalance, and coverages were determined by timed exposure to the source. Typical rates were 0.2-0.5 Å/minute. Based on prior experience with the deposition equipment used it is expected that absolute coverages were accurate to about 25%. All exposure to B₂O₃ was done with samples held at between 550 and 600°C. After deposition, samples were annealed to temperatures between 600 and 1150°C as required. Samples were cooled to room temperature for both STM and LEED measurements.

Results

Figure 1 is a schematic showing the LEED patterns over the full range of annealing temperatures and B coverages studied, as well as circles indicating the conditions under which the surfaces shown here were prepared. Circles linked by arrows indicate a sequence of annealings or depositions on the same sample. B coverages are labeled in terms of total deposited B₂O₃ layer thickness before annealing. A scale in terms of monolayers (where 1 ML = 7.8×10^{14} atoms/cm² = surface atomic density of the unreconstructed Si(111) surface) is not given here since the yield of B remaining on the surface per deposited B₂O₃ molecule was not quantified. Any further statements of B coverage in ML given in this paper are deduced from the number density of B or Si related features in the images, and are to be distinguished from the amount of B₂O₃ deposited which is always given in Å.

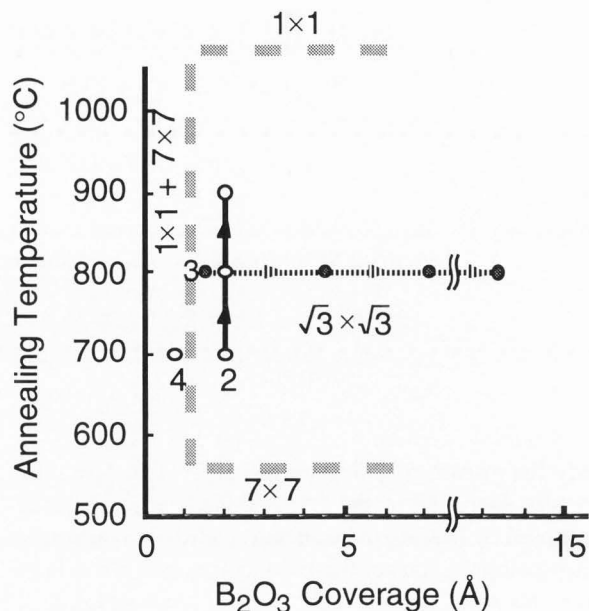


Figure 1. A phase diagram showing LEED patterns for B on Si(111) as a function of B₂O₃ deposition and annealing temperature. No ordered phases are seen by LEED aside from 7×7 and $\sqrt{3} \times \sqrt{3}$. Circles show the preparation conditions for surfaces shown in the other figures, and the starting points for the sequences shown in Figures 2 and 3 are labelled by number, as is the point representing the surface in Figure 4.

From these measurements and others not shown in Figure 1, it is possible to make the following general observations. At least 2-3 Å of B₂O₃ is necessary to produce a saturated $\sqrt{3}$ surface. Also, it is necessary to anneal the surface to 600°C to convert the surface to the $\sqrt{3}$ structure. Surfaces annealed to 550°C or less show either a diffuse 7×7 or 1×1 LEED pattern, depending on the initial B₂O₃ coverage. Core level photoemission shows that 700°C is sufficient to drive the O from the surface (Cao *et al.*, 1993). The optimal conditions for forming a well-ordered $\sqrt{3}$ surface are at about 3-5 Å B₂O₃ coverage, and an annealing temperature of 800°C. Annealing at 800°C or above drives some of the B away from the surface. However, the $\sqrt{3}$ LEED pattern is stable up to 1100°C. It is not possible to restore the clean Si(111) 7×7 LEED pattern except by extended annealing at above 1200°C, and even in these cases, STM shows the presence of some B on the surface as will be described later.

Figures 2a, 2b, and 2c show the evolution of a surface with 2 Å coverage after annealing at 700, 800, and 900°C respectively. Each of these STM images is 250 × 250 Å in size and shows the unoccupied states of the sample. All three of these surfaces showed a sharp

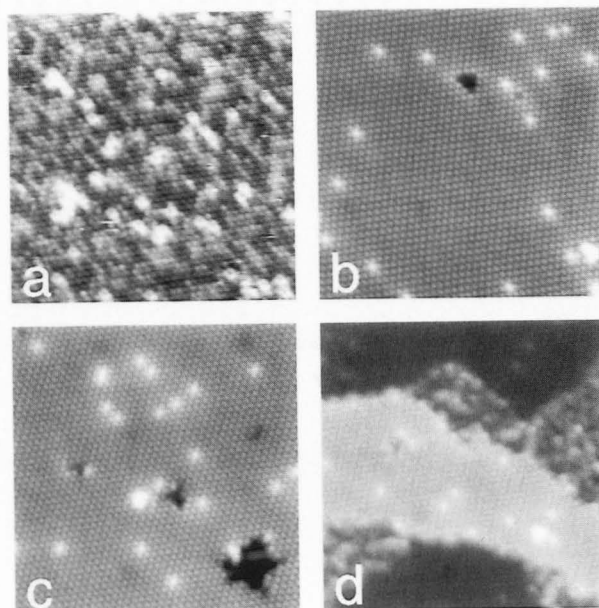
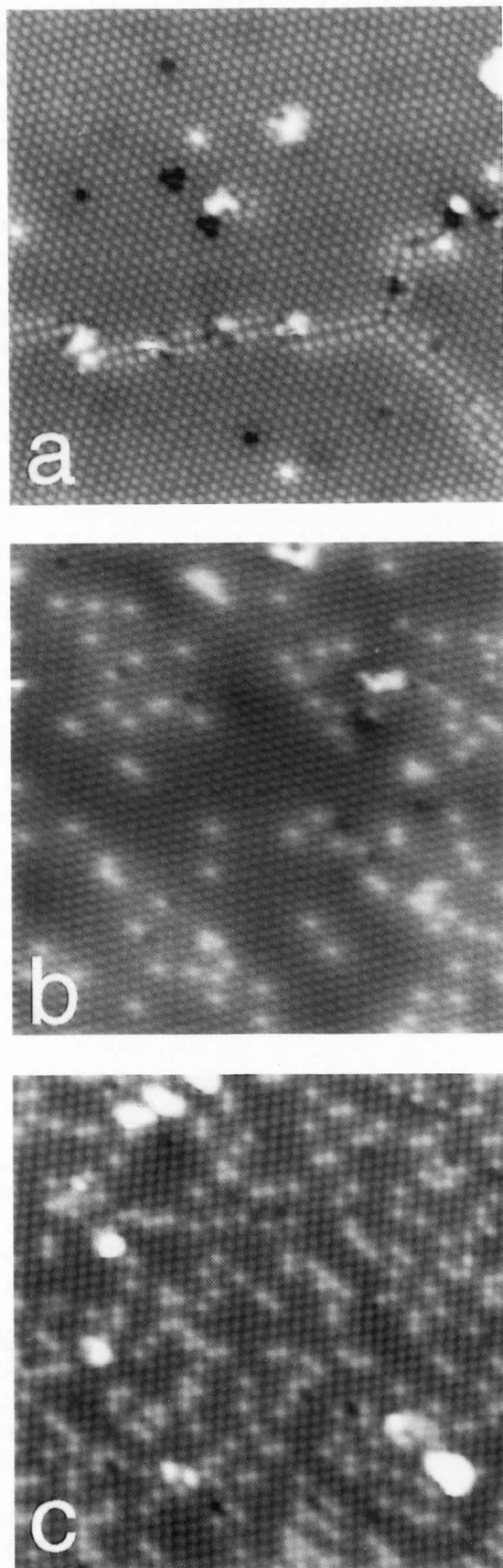


Figure 3. A sequence of 250 Å × 250 Å images showing a surface as a function of deposited B₂O₃. The coverages are (a) 1.5 Å, (b) 4.5 Å, (c) 7.1 Å, and (d) 13.3 Å. The sample was annealed at 800°C between depositions. Panel (b) represents the most defect-free $\sqrt{3} \times \sqrt{3}$ surface, whereas (a) is B deficient and (c,d) show effects of excess B.

 $\sqrt{3}$ LEED pattern. The STM images also show well-ordered $\sqrt{3}$, with the characteristic one maximum per unit cell as per earlier work (Bedrossian *et al.*, 1989; Lyo *et al.*, 1989). At 700°C (Fig. 2a), the surface shows a network of domain boundaries that are typically 200-300 Å apart. Aside from these domain boundaries, there is also a small population (< 0.01 ML) of bright dots and dark missing spots. Annealing to 800°C removes almost all of the extended domain boundaries, and increases the population of bright defects. Annealing to 900°C further increases the population of bright defects to about 20% of the maxima (≈ 0.06 ML). Previous work has associated the darker maxima with Si adatoms in T₄ sites over B atoms (i.e., the standard $\sqrt{3}$ structure) and the brighter maxima can be associated with Si adatoms without the underlying B (Bedrossian *et al.*, 1989; Lyo *et al.*, 1989).

Figures 3a, 3b, 3c, and 3d show the evolution of the

Figure 2 (at left). A sequence of 250 Å × 250 Å images showing a surface with 2 Å deposited B₂O₃, annealed at (a) 700°C, (b) 800°C, and (c) 900°C. The number of bright defects in the $\sqrt{3} \times \sqrt{3}$ phase increases with annealing temperature.

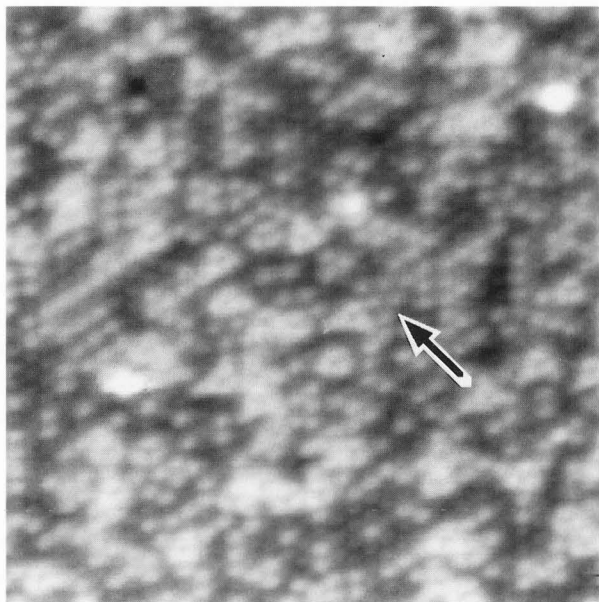


Figure 4. A 200 Å × 200 Å image of a surface prepared at 0.75 Å coverage and annealed at 700°C. The surface shows predominantly $\sqrt{3} \times \sqrt{3}$ ordering, but other periodicities are present. The arrow shows six adatoms in a $p(2 \times 2)$ arrangement.

same sample after sequential depositions of 1.5, 4.5, 7.1, and 13.3 Å of B₂O₃. All depositions were done with the sample held at 570°C, and each incremental deposition was followed by annealing the sample to 800°C for 15 minutes. Figure 3a shows the surface below the saturation coverage. The overall surface structure is $\sqrt{3}$ but there is a large population of both bright and dim maxima in the structure. As in Figure 2, the brightness of the maxima depends on the presence or absence of subsurface B. About 70% of the maxima are dark, which is consistent with the fact that the B₂O₃ coverage is between 50 and 75% of saturation. In addition to the $\sqrt{3}$ structure, there are a number of bright ring-shaped features, as well as larger, irregular clusters. Figure 3b shows the surface at 4.5 Å which is definitely above the saturation coverage. The predominant defect is the single bright maxima. The density of this features is much less than that for the 2 Å sample annealed at 800°C (Fig. 2b). This image is characteristic of the structural perfection of the entire surface prepared under these conditions. At 7.1 Å (Fig. 3c), the surface is largely unchanged, indicating that the B coverage has saturated and that additional B deposition has had very little effect on the surface. However, there is a slight increase in the number of irregular holes in the surface. This image shows the typical size of such a hole. The

bottoms of these holes show the $\sqrt{3}$ structure. Finally, at 13.3 Å, there is clear evidence of excess B accommodation at the surface. Figure 3d shows a region with a narrow terrace running as a horizontal stripe across the image. The lowest and highest terrace in the image show the $\sqrt{3}$ structure as before; these terraces are 3.1 Å apart in height which corresponds to a bilayer step on Si(111). At the step edges on either side of the stripe, there are areas at an intermediate height that appear to be disordered. These areas show local $\sqrt{3}$ structure but they are laced with domain walls. Elsewhere on the same surface, there is also an increase in the density of the holes shown in Figure 3c. The floor of the holes is at a similar depth below the surrounding terrace (1-2 Å depending on sample bias) as the islands at step edges are below the adjacent upper terrace. The details of these new structures associated with excess B will be discussed elsewhere.

Figure 4 shows a surface after 0.75 Å deposition and annealing at 700°C. This image is at a slightly higher magnification than the others and spans 200 × 200 Å. The ratio of brighter to darker $\sqrt{3}$ maxima is higher than at 1.5 Å, and there is a much higher density of ring-shaped features. Both of these characteristics are due to the lower concentration of B at the surface. Numerous slips in the $\sqrt{3}$ periodicity are visible upon close inspection. There are also a few areas where adatom related features are arranged in 2×2 patterns rather than $\sqrt{3}$. One such area is marked by the arrow. The ordering is still largely $\sqrt{3}$ as is evidenced by the LEED patterns from such surfaces. This type of surface structure is also seen on samples that have been heated at up to 1150°C, where much of the B is believed to have left the surface region. It is not possible to say on the basis of these measurements whether the B has evaporated or has diffused into the bulk. Shen *et al.* (1994) have shown that at lower B concentrations than what is shown here, the surface has adatoms arranged in a mixture of 2×2 , $c(4 \times 2)$ and $\sqrt{3} \times \sqrt{3}$ arrangements, along with a high density of the ring features, and that LEED patterns of such a surface are diffuse 1×1 (Shen *et al.*, 1994). Similar rings and disordered adatom arrangements have been seen on clean Si(111) surfaces that were quenched from the high temperature 1×1 phase (Yang and Williams, 1994). In this case, the surface structure is attributed to an excess population of Si adatoms frozen in by the quenching. A similar explanation is applicable to the sub-saturation B/Si(111) surface shown in Figure 4; B displaces Si and thus raises the population of adatoms above that of the 7×7 surface, and this excess is accommodated by the formation of the 1×1 phase. One difference between the surface with and without B is that the Si(111) 1×1

shows only one type of adatom, whereas the B 1×1 clearly shows two types of adatoms that are due to the presence and the absence of sub-surface B.

Conclusions

In summary, B/Si(111) surfaces prepared by B₂O₃ deposition and heating have been studied by STM over a wide range of B₂O₃ coverage and annealing temperature. Over most of the range studied, the surface structure is the well-known B-induced $\sqrt{3} \times \sqrt{3}$ phase which is associated with 1/3 ML of B. This structure requires at least 2-3 Å of B₂O₃ and annealing at 600°C or above. The optimal conditions to produce a well-ordered $\sqrt{3} \times \sqrt{3}$ surface are 3-5 Å deposited B₂O₃ and an annealing temperature of 800°C. At higher temperatures, there is some B desorption, but the $\sqrt{3} \times \sqrt{3}$ LEED pattern is stable at temperatures up to 1100°C, depending on the initial B coverage.

The results for B saturated samples annealed to 900°C and above are in agreement with previous work on samples prepared by B dopant segregation. However, the advantage of B₂O₃ deposition over B segregation is the ability to prepare surfaces well away from the conditions for the ideal surface. At low temperatures (570-600°C), there may be other possible B bonding sites (Cao *et al.*, 1993; Lyo *et al.*, 1989). Excess B₂O₃ deposition (three to four times the saturation coverage) leads to new phases that may be associated with the accommodation of excess B. Both of these regions of the phase diagram will be the objects of further study.

Acknowledgements

This research was supported by the National Science Foundation (DMR-9223764) and the Petroleum Research Fund which is administered by the American Chemical Society. The Stanford Synchrotron Radiation Laboratory is supported by the Department of Energy, Office of Basic Energy Sciences and Office of Health and Environmental Research.

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Discussion with Reviewers

Reviewer I: The authors claim the light and dark spots are due to the presence or absence of subsurface B. This is the most likely explanation but is there any evidence to support this assertion?

Authors: We have cited the assignment of light and dark spots as per prior STM work by others. As noted in the text, when the surface is depleted of B by high temperature annealing, the density of bright defects increases which is consistent with their being associated with B deficiency.

I.S.T. Tsong: The authors mention 2×2 features in Figure 4. Perhaps the authors should point out that there is more than one type of 2×2 reconstruction.

Authors: We have changed the notation from 2×2 to p(2×2) to be more precise.

M. Trenary: Do the authors have any information on the chemical reactions associated with the conversion of B₂O₃ to B on the Si surface?

Authors: The nature of the reaction does not affect the conclusions of this paper, although it may have some influence on the large scale structure of the surface. Prior work by other techniques has shown that the reaction involves etching of Si, which desorbs as SiO (Tuppen *et al.*, 1988). This could influence surface structure, particularly in the excess B regime. These results will be published elsewhere.

Additional References

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