

AD-A279 819



U.S. OFFICE OF NAVAL RESEARCH

GRANT N00014-91-J-1629

R&T Code 413S001

Technical Report #18

Accession For	
NTIS	CRA&I ☒
DTIC	TAB ☐
Unannounced ☐	
Justification	
By _____	
Distribution /	
Availability Codes	
Dist	Avail and/or Special
A-1	

**An Atomically-resolved STM Study of the Interaction of Phosphine (PH₃)
with the Si(001) Surface**

by

Y. Wang, M.J. Bronikowski, and R.J. Hamers

Prepared for Publication

in

Journal of Physical Chemistry

May 10, 1993

Department of Chemistry
University of Wisconsin-Madison
Madison, WI 53706

DTIC
ELECTE
JUN 02 1994
S G D

Reproduction in whole or in part is permitted for any purpose of the United States Government.

This document has been approved for public release and sale: its distribution is unlimited.

DTIC QUALITY INSPECTED 2

94 6 1 051

2196
94-16327

REPORT DOCUMENTATION PAGE			FORM 486-103 DAB NO 0004-0188	
2. The report should be prepared by the person or persons who are responsible for the collection of information. It should include the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.				
1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE 5/27/94	3. REPORT TYPE AND DATES COVERED Interim 6/1/93-5/31/94		
4. TITLE AND SUBTITLE An Atomically-Resolved STM Study of the Interaction of Phosphine (PH ₃) with the Silicon (001) Surface			5. FUNDING NUMBERS Grant N00014-91-J-1629 R&T Code 413S001	
6. AUTHOR(S) Y. Wang, M. J. Bronikowski and R. J. Hamers				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Department of Chemistry University of Wisconsin-Madison 1101 University Avenue Madison, WI 53706-1396			8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research, Chemistry 800 North Quincy Street Arlington, VA			10. SPONSORING/MONITORING AGENCY REPORT NUMBER 18	
11. SUPPLEMENTARY NOTES				
12a. DISTRIBUTION/AVAILABILITY STATEMENT Unlimited			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) The interaction of phosphine (PH₃) with the Si(001) surface has been investigated with scanning tunneling microscopy. At 300 K, PH₃ adsorbs molecularly on top of a single Si-Si dimer with the phosphorus atom in a pentacoordinate configuration. Phosphine adsorption is accompanied by occasional ejection of silicon atoms from the substrate onto the surface, creating surface vacancies and Si adatoms. Si atoms are preferentially ejected from defect sites. At high coverage, adsorbed PH₃ molecules order into small regions of c(4x2) symmetry and the ejected silicon nucleates into small dimer strings. The long-range order of the molecular PH₃ is disrupted by domain boundaries and the ejected silicon. Annealing PH₃-saturated surfaces produces further ejection of silicon onto the surface, resulting in large silicon islands covering approximately 20% of the surface.				
14. SUBJECT TERMS			15. NUMBER OF PAGES 37	
			16. PRICE CODE ---	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT UL	

**An Atomically-Resolved STM Study
of the Interaction of Phosphine (PH₃)
with the Silicon (001) Surface**

Yajun Wang, Michael J. Bronikowski, and Robert J. Hamers*

Dept. of Chemistry
Univ. of Wisconsin
1101 University Avenue
Madison, WI 53706

E-mail: HAMERS@BERT.CHEM.WISC.EDU

Abstract

The interaction of phosphine (PH₃) with the Si(001) surface has been investigated with scanning tunneling microscopy. At 300 Kelvin, PH₃ adsorbs molecularly on top of a single Si=Si dimer with the phosphorus atom in a pentacoordinate configuration. Phosphine adsorption is accompanied by occasional ejection of silicon atoms from the substrate onto the surface, creating surface vacancies and Si adatoms. Si atoms are preferentially ejected from defect sites. At high coverage, adsorbed PH₃ molecules order into small regions of c(4x2) symmetry and the ejected silicon nucleates into small dimer strings. The long-range order of the molecular PH₃ is disrupted by domain boundaries and the ejected silicon. Annealing PH₃-saturated surfaces produces further ejection of silicon onto the surface, resulting in large silicon islands covering approximately 20% of the surface.

* Author to whom correspondence should be addressed.

Introduction

Phosphine (PH₃) is a molecule widely used in chemical vapor deposition (CVD) processes for n-type doping of silicon¹⁻⁷ and for the bulk growth of III-V semiconductors such as InP.⁸ In Silicon CVD, it is widely known that the presence of even small amounts of PH₃ strongly influences the growth kinetics of silicon CVD processing.^{1-3,9} Presumably through the formation of a phosphorus-passivated surface. Yet, little is known from a fundamental standpoint about how PH₃ interacts with silicon surfaces, how it dissociates on the surface, or how phosphorus atoms are incorporated into the silicon lattice.

Van Bommel, et al.¹⁰ first studied the interaction of PH₃ with Si(111) surface using low-energy electron diffraction (LEED) and Auger electron spectroscopy (AES). Bozso and Avouris¹¹ and, more recently, Yates and co-workers¹²⁻¹⁴ have studied the interaction of PH₃ with the Si(111)-(7x7) surface using a variety of techniques including photoemission, high-resolution electron ion scattering spectroscopy (ISS), high-resolution electron energy-loss spectroscopy (HREELS), temperature-programmed desorption (TPD), and electron-stimulated desorption (ESD). On Si(111), they concluded that PH₃ adsorbs with a sticking coefficient of near unity, producing both adsorbed PH₃ molecules and partially-dissociated PH_x fragments.

Although the Si(001) surface is by far more technologically relevant than the Si(111) surface, comparatively little is known about how PH₃ interacts with Si(001). Yu, Meyerson, and co-workers^{9,15,16} used SIMS, AES, XPS, TPD, and LEED measurements to study the interaction of PH₃ with Si(001). They found that PH₃ adsorption on Si(001) was mostly molecular at room temperature with a sticking coefficient of near unity, and that PH₃ molecules desorbed at 550 Kelvin with an activation barrier of approximately 0.6 eV¹⁶. At room temperature, PH₃-exposed surfaces retained an ordered (2x1) LEED pattern even at saturation coverage.¹⁵ Based on these results, they proposed¹⁶ that PH₃ adsorbed molecularly in a

configuration in which the "lone pair" orbital interacted with the two dangling bonds of a Si=Si dimer. They found that annealing PH₃-exposed surfaces to 475 Kelvin induced partial dissociation of PH₃, leaving hydrogen atoms on the Si substrate. As the temperature was increased to 675 Kelvin, hydrogen desorbed from the surface, and the saturation coverage of phosphorus increased simultaneously due to the increased availability of surface sites, reaching a maximum coverage at 825 Kelvin which was approximately four times the room-temperature value and which corresponded to one full monolayer of adsorbed phosphorus. At still higher temperatures, they found that the coverage decreased due to the desorption of P₂.

In this study, we report the first atomic-resolution study of the interaction of PH₃ with the Si(001) surface using Scanning Tunneling Microscopy (STM). Our studies reveal that at room temperature, molecules of PH₃ bond to the Si(001) surface directly above a Si=Si dimer, with the phosphorus atom effectively becoming pentacoordinate. At higher coverage, these molecules order into small domains with a local c(4x2) configuration at room temperature. We also find that the exothermicity of the adsorption process is sufficiently high to eject silicon atoms from the substrate lattice, creating new substrate defects and enlarging existing defects during simple room-temperature adsorption. Annealing PH₃-exposed surfaces produces extensive Si atom ejection which roughly corresponds to ejection of one silicon atom for each initially-adsorbed PH₃ molecule, suggesting that the phosphorus atoms readily displace Si atoms from the outermost surface layer at elevated temperatures.

Experimental

STM experiments were performed in an ultrahigh vacuum chamber with a base pressure of below 1x10⁻¹⁰ torr. Wafers of n-type Si(001) oriented to within 0.5° were used. Wafers were obtained from Virginia Semiconductor and from Wacker Chemitronic, with the latter showing lower defect concentrations but otherwise identical behavior. Samples were prepared by first degassing for about 10 hours at 900 Kelvin, then annealing to 1400

Kelvin for several seconds on a separate heating stage. After allowing 30 min for cooling to room temperature, samples were transferred to the STM and imaged to ensure that the starting surface was clean and well ordered. Samples were exposed to high-purity PH₃ (99.999%, Matheson) as indicated in the individual experiments below. To avoid spurious decomposition of PH₃, no filaments were lit during or after PH₃ exposure. Exposures were determined using the ion pump current reading to indicate pressure, which was previously calibrated against an ion gauge. All images were acquired in the constant current mode using a tunneling current of less than 1.0 nA and a range of bias voltages between -3V (probing filled states) and +3V (probing empty states).

Results

Fig 1a shows an STM image of the Si(001) surface before exposure to PH₃, acquired at -2V sample bias. The rows of Si=Si dimers are clearly visible in this image, although the individual dimers are not easily resolved at this resolution. In addition to the rows of dimers, this image shows a second characteristic of the Si(001) surface, which is the presence of defects of various types, primarily consisting of vacancies and vacancy clusters.^{17,18} Defects on this surface are caused by a combination of factors including chemical "etching", impurities, and possibly, spontaneous vacancy formation at higher temperatures, and the concentration of defects depends on the sample preparation procedure. The image chosen for fig. 1a shows a rather high concentration of defects, in order to better illustrate one feature of PH₃ adsorption. After acquiring this image, the tip was withdrawn from the surface about 1μm, the bias was reduced to zero, and the sample was exposed to 0.06 Langmuir PH₃. The bias voltage was then re-applied, the tip was brought back into tunneling, and the same region of the surface was again imaged, as shown in fig. 1b.

A comparison of fig. 1a and 1b shows two primary changes. The first obvious change produced by PH₃ exposure is the appearance of small protrusions in fig. 1b, which appear higher (whiter in the grayscale representation). A second change is that in some of the regions which were defect-free before exposure to

PH₃, there now appear to be vacancy defects; one example of a region in which a vacancy was created is outlined in fig. 1 with a rectangular box. Even more often, we find that the existing small "atomic-sized" defects typical of fig. 1a are now replaced by larger defects, many of which appear to be vacancy clusters of 6-10 missing dimers each. For example, in fig. 1a, several "C"-type defects,¹⁸ each of which appears as two missing atoms in adjacent dimers within a single dimer row, are indicated as "C". After PH₃ exposure, fig. 1b shows that each of these same areas now appears to have lost two more Si atoms, becoming a two-dimer (four-atom) surface vacancy. We also note that because the "C" defect breaks the mirror plane symmetry along the Si=Si dimer bond, fig. 1a shows that this defect induces dimer tilting (buckling) in the surrounding regions; in contrast, in fig. 1b the tilting is gone because removal of two more atoms restores the mirror-plane symmetry. While the apparent creation of vacancies might be attributed to electronic structure changes produced by PH₃ adsorption or decomposition, we rule out such an interpretation based on the data to be shown below as well as quantitative measurement of the depth of these newly-created "vacancies" which show them to have a depth of 1.4 Å, very close to the 1.36 Å Si(001) step height, over the entire range of bias voltages between -3 V and +2.5 V. This strongly suggests that these features are indeed vacancies in the outermost atomic layer created by the interaction with PH₃.

To understand the nature of the adsorption features, the appearance of the protrusions produced by PH₃ exposure has been studied using high-resolution STM imaging at both positive and negative sample bias. At high negative sample bias, as in fig. 2a (-2.8 V), the protrusions can be clearly divided into two types based on their shape. One type, labeled "A", appears elongated, while a second type, labeled "B", appears to be round. Fig. 2b shows the symmetry of these features and the height profiles measured across them, along the lines indicated in fig. 2a. The distinction between the "A" and "B" features is even more obvious by comparing images acquired at negative and positive bias, as shown in fig. 2c (-2V sample bias) and 2d (+2V sample bias). At a bias voltage of -2V

(2c), the difference in shape between "A" and "B" can still be detected, but is not as obvious as at higher negative voltage, as in 2a. Lines are drawn in fig. 2c showing that both "A" and "B" are maximized directly over the center of a Si=Si dimer. At positive sample bias, fig. 2d shows that the "A" features again appear as protrusions (now almost round), but the "B" features appear as depressions. While fig. 1 and 2 were obtained on surfaces with moderately high defect concentrations, experiments on surfaces with smaller numbers of defects show that the number of "A" features correlates with the defect density, while the number density of "B" features correlates directly with the PH₃ exposure. This strongly suggests that the "A" features are ejected silicon, while the "B" features arise from the adsorbed PH₃ molecules.

Previous studies by Yu, et al.^{15,16} indicated that PH₃ adsorption on Si(001) at room temperature was primarily molecular, with little or no dissociation at room temperature. Our STM images after room-temperature PH₃ exposure do not show any features identifiable as H atoms adsorbed on the Si dimers, either as individual adsorbed atoms or as adsorbed H atoms "paired" on the Si dimers in the Si(001)-(2x1)H monohydride phase. As previously shown by Boland,¹⁹ H atoms bond to a single "dangling bond" of a Si=Si dimer, breaking the weak π bond but leaving the strong σ bond intact, and leaving the remaining Si bond only three-fold coordinate with a "dangling bond". The Si-H electronic states are far from the Fermi energy (E_F). Because this dangling bond lies at E_F electrons can readily tunnel both into and out of the Si dangling bond, while the Si-H states are far from the Fermi energy. As a result, STM images of hydrogen atoms adsorbed on Si(001) show a depression at the location of the H atoms, but a protrusion at the location of the remaining dangling bond. It is important to recognize that such "dangling bonds" are located to the side of the dimer and not directly on top of the dimer; therefore, features "A" and "B" cannot be attributed to Si "dangling bonds". Likewise, we previously²⁰ investigated in detail the Si(001)-(2x1)H monohydride phase of adsorbed H and find that neither of these features corresponds to this phase. We therefore conclude that, in

agreement with the previous results of Yu,¹⁶ there is little or no dissociation upon PH₃ adsorption on Si(001) at room temperature.

In order to investigate the thermal stability of these features, we obtained STM images on samples exposed to PH₃ at room temperature and then annealed to 500 Kelvin for 30 seconds. While the details of the thermal dissociation will be discussed elsewhere, figure 3 shows that this thermal annealing induces several changes in the appearance in the surface. After annealing, the features identified as "A" are completely gone, a few features identified as "B" remain, and small regions of the surface show the structure characteristic of the Si(001)-(2x1)H monohydride structure, in which one hydrogen atom bonds to each of the two dangling bonds of a Si=Si dimer, forming a unit of stoichiometry H-Si-Si-H. We have previously published a detailed study of the appearance and identification of hydrogen in the monohydride phase using STM in reference ²⁰. When in the monohydride structure, it is possible to quantify the amount of surface hydrogen, as discussed below.

Another change produced by thermal annealing is the appearance of surface structures which appear to be small islands of adsorbed epitaxial silicon. Fig 3a and 3b show filled-state (3a, -2V) and empty-state (3b, +2V) STM images of a single region of a Si(001) surface which was exposed to 0.04 L PH₃ at 300 Kelvin, then annealed to 500 K for 30 seconds, and then cooled to 300 Kelvin for imaging. These images show elongated protrusions which reach a maximum at a point located midway *between* two dimers within a single dimer row, and located on a line bisecting the dimer row. At both positive and negative sample bias, these features are $1.4 \pm 0.1 \text{ \AA}$ higher than the surrounding terrace. In unfilled state images (3b, +2V), these same features are resolved into two well-separated "lobes". The appearance of these features, and the variation in appearance with applied bias, is identical to that observed for Si=Si dimers²¹. At negative bias electrons tunnel out of the occupied π orbital giving the dimers an oval shape, while at positive bias electrons tunnel into the empty π^* antibonding orbital, which has a node in the center and leads to a splitting of

the dimer into two well-resolved protrusions. Separate measurements both on individual silicon dimers and small islands of epitaxial silicon prepared by thermal decomposition of disilane^{20,22} show that such dimers appear $1.4 \text{ \AA}$ higher than the underlying terrace and, at positive sample bias, split into two lobes separated by $5.5 \pm 0.2 \text{ \AA}$, in excellent agreement with the appearance of the features described above. That the structures indicated in fig. 3 are Si=Si dimers is further supported by the appearance in fig. 3a and 3b (near the bottom, labeled "DS") of a longer dimer "string" again showing the bean-shaped appearance at negative bias but a splitting with maxima separated by $5.5 \text{ \AA}$ at positive bias. An even larger dimer island found on the annealed, PH₃-exposed Si(001) surface is shown in fig. 3c and 3d, again showing the bias-dependent changes in appearance between negative bias (3c, -2V) and positive bias (3d, +2V) characteristic of epitaxial Si=Si dimers. The dimers observed in these figures are identical in every respect with Si=Si dimers prepared by chemical vapor deposition and by molecular beam epitaxy. We further note that in other experiments, to be published separately, we have observed and studied dimers produced by thermal decomposition of PH₃ on Si(001) to form P-P dimers and Si-P dimers at higher temperature; those experiments show very pronounced differences between the appearance of Si=Si, Si-P, and P-P dimers on Si(001) and confirm that the dimers observed in fig. 3 are indeed dimers of silicon, the structures labeled "D" in fig. 3a and 3b are individual Si=Si dimers, and the structures labeled "DS" in 3a-3d are Si=Si dimer strings. As described below, although most of the silicon observed after room-temperature exposure at low coverage is in the form of individual Si adatoms, as the coverage of PH₃ is increased more of the Si is found in the form of Si=Si ad-dimers even at room temperature.

Based on the above results, we conclude that feature "A" is an individual Si adatom, and feature "B" is an adsorbed molecule of PH₃. This conclusion is further validated on the basis of counting statistics obtained on a number of images of total area $80,000 \text{ \AA}^2$ before and after annealing. Errors are estimated as the square root of the number of observed features. After room temperature

exposure to 0.04L PH₃, the number density of features designated as "A" was $(5.5 \pm 1.0) \times 10^{12} \text{ cm}^{-2}$ and the number of features designated as "B" was $(1.0 \pm 0.2) \times 10^{13} \text{ cm}^{-2}$. As noted above, the ratio of "A" to "B" feature depends on the surface quality, with "B" features always more common than "A" features and the "A" features more commonly observed on defected surfaces than "ideal" surfaces. After annealing, the number density of hydrogen atoms in the monohydride structure was $(3.2 \pm 0.5) \times 10^{13} \text{ H atoms/cm}^2$, while counting the number of silicon atoms present in the form of "ad-dimers" was $(6.1 \pm 1) \times 10^{12} \text{ Si atoms/cm}^2$. Thus, the ratio of "B" features (before annealing) to H atoms (after annealing) is 3.2, close to the value of 3:1 expected for complete dissociation if feature "B" is in fact a molecule of PH₃. Likewise, the number of "A" features before annealing is close to the number of silicon atoms present as epitaxial ad-dimers after annealing, supporting the interpretation of the "A" feature as arising from a single adsorbed Si atom.

This interpretation is further supported by measurements showing that the at higher exposure the number density of "B" features continually increases, and that these features show local ordering. In previous experiments of PH₃ adsorption on Si(001) by Yu and Meyerson^{15,16}, an ordered (2x1) LEED pattern was observed after saturation exposure of Si(001) to PH₃. To investigate the ordering of PH₃ molecules on the surface, we also conducted experiments of room-temperature adsorption at different coverages. Figure 4a shows a Si(001) surface after exposure to 0.6 L PH₃ at room temperature. Clear ordering of the adsorbates can be observed, ordering first along the dimer rows with a spacing 2a₀ (where a₀=3.85 Å), and at higher coverage showing ordering between dimer rows. Images at positive bias confirm that these ordered adsorbates are indeed the "B" features attributed to molecules of PH₃. Fig. 4b shows a larger image at this same coverage. Ordering between the dimer rows virtually always occurs with the PH₃ groups staggered to form small regions of c(4x2) symmetry, as depicted in the model in fig. 4c. In this c(4x2) structure the local coverage is 0.25 monolayer.

Continued exposure of the Si(001) surface to PH₃ ultimately produces a saturated surface which is shown in fig. 5a (4 L exposure, -2V sample bias). This large image again shows ordering of the PH₃ adsorbates into a c(4x2) geometry. Fig. 5b shows a high-resolution image of a saturated surface showing in more detail the c(4x2) arrangement. The c(4x2) arrangement is strongly preferred over all other arrangements, as no regions of other structure, such as p(2x2) or (2x1), are ever observed. In the previous study by Yu and Meyerson¹⁵, it was reported that the sharp (2x1) LEED pattern characteristic of the Si(001) starting surface was retained after saturation exposure to PH₃, but the relative intensities of the spots were changed. Our results show that the ordering is actually c(4x2); however, the long-range order of the surface produced by room-temperature adsorption is frequently disrupted by domain boundaries between c(4x2) domains as well as ejected silicon, so that the domains of c(4x2) typically are smaller than 50 Å in extent. Because this domain size is smaller than the typical coherence length of the electron beam in LEED, the individual domains do not give rise to well-defined c(4x2) LEED pattern and only second-order spots would be expected, consistent with the observations of Yu, et al.^{9,15,16}. We note that on the basis of Auger measurements, Yu, et al.^{9,15,16} concluded that the saturation coverage of phosphorus (as PH₃) on the Si(001) surface at room temperature was 1/4 monolayer, in excellent agreement with the total coverage expected from ordering of PH₃ molecules into a c(4x2) overlayer.

At saturation exposure, we also find that much of the ejected silicon has nucleated into small dimer strings, as indicated by the arrow in fig. 5c, even though the temperature of the sample has not been raised. We believe the growth into small dimer strings and small islands at room temperature can be attributed to the room-temperature diffusion of Si adatoms ejected by the PH₃ adsorption as well as possible enhancement of surface diffusion by the exothermicity of the PH₃ adsorption.

If a sample which has been exposed to saturation coverage of PH_3 is heated, the decomposition of the PH_3 produces elemental phosphorus and hydrogen. Hydrogen desorbs from the surface, while phosphorus can diffuse into the Si lattice or can desorb from the surface as PH_3 or P_2 . Fig. 6 shows a $\text{Si}(001)$ surface exposed at room temperature to PH_3 , and then annealed under UHV conditions to a temperature of 950 Kelvin for 150 seconds. The results of Yu, et al.,^{9,15} as well as our own Auger measurements, indicate that under these conditions all phosphorus initially adsorbed on the surface has either desorbed from the surface or diffused into the bulk. As shown in fig. 6, surfaces prepared in this manner again clearly show the effects of silicon ejection through the formation of large silicon islands on the surface. Further experiments to be published elsewhere²³ allow us to distinguish between $\text{Si}=\text{Si}$, $\text{Si}-\text{P}$, and $\text{P}-\text{P}$ dimers on the surface and confirm that the islands shown in fig. 6 are nearly pure silicon and are not $\text{P}-\text{Si}$ alloy. By calculating the fractional surface covered by islands in a number of large-area scans, we have determined that 20% of the surface area is covered by Si atoms which, presumably, are ejected either in the initial adsorption or through the displacement of substrate Si atoms by phosphorus during the heating. As noted earlier, the amount of Si ejected during room-temperature adsorption of PH_3 is always less than 1 Si per PH_3 molecule, and the number of ejected Si atoms is more typically only 20-30% of the number of adsorbed PH_3 molecules. Since the saturation coverage of PH_3 is no higher than 0.25 monolayer (to form a perfect $c(4 \times 2)$ overlayer), almost all of the silicon ejection required to produce these islands must occur during the annealing process, rather than from the room-temperature Si ejection. This indicates that the overall process of PH_3 decomposition followed by phosphorus desorption must involve substantial displacement of Si atoms from the outermost silicon surface layer, which likely arises from the substitution of P atoms for Si sites in the outermost surface layer. This process is similar to the interfacial mixing found by Tromp and Reuter²⁴ for arsenic on $\text{Si}(001)$. Further experiments will be required to determine the exact mechanism by which these Si atoms are produced.

Discussion

a) Identification of surface species:

Our experimental results prove several important facts which are crucial in identifying species "A" and "B". First, we note that we do not observe individual adsorbed hydrogen atoms or the $\text{Si}(001)-(2 \times 1)\text{H}$ monohydride structure on the surface after PH_3 adsorption at room temperature, thereby demonstrating that PH_3 adsorbs molecularly. Secondly, we observe the creation of vacancies, so that in order to conserve mass we must have silicon present on the surface as adatoms, ad-dimers, or other chemical form. The symmetry of the "A" and "B" species does not correspond to the well-known symmetry of the $\text{Si}=\text{Si}$ dimers, and so the primary surface species are expected to be PH_3 molecules and Si adatoms. The correlation between the number of "A" features and the number of created vacancy defects implies that "A" arises from silicon. The annealing experiments show that the number of silicon atoms in the form of dimers after annealing is nearly identical to the number of features identified as "A" before annealing, thereby indicating that each "A" is indeed one silicon atom. Likewise, the "B" features are by far the predominant species present after adsorption on nearly defect-free surfaces (as in fig. 2a) and at high coverage. Since there is no evidence for PH_3 dissociation at room temperature, we conclude that each "B" is an adsorbed PH_3 molecule, and feature "A" is an individual Si atom produced by ejection from the terrace. Figure 7 shows the proposed bonding configurations for these two species on the $\text{Si}(001)$ surface, along with the most common configuration for an ad-dimer.

In previous studies^{22,25} we have applied the principles of coordination chemistry to identify molecular fragments such as SiH_3 and SiH_2 on $\text{Si}(001)$ surfaces, showing that these SiH_x fragments adopt geometries which optimize 4-fold coordination of the Si atoms. Because of the small electronegativity difference between Si and P, we expect $\text{Si}-\text{P}$ bonds to be nearly covalent, so that these same principles should apply. Unlike silicon, however,

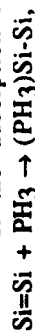
the phosphorus atom has low-lying d states which it can utilize to hybridize in a sp^3d configuration, in addition to the sp^3 configuration it adopts in compounds such as PH_3 .²⁶ As a result, phosphorus can form compounds with many elements both in coordination 3 and coordination 5, such as PCl_3 and PCl_5 . In the interaction of PH_3 with Si, we can consider that adsorption might be dissociative, breaking P-H bonds in order to form Si-P and Si-H bond, or it might be molecular. Our results indicate that adsorption of PH_3 on the Si(001) surface is indeed molecular, involving a transformation from coordination number 3 to coordination number 5 for the phosphorus atom.

In principle, the P atom in an adsorbing PH_3 molecule can achieve 5-fold coordination on the Si(001) surface in several ways, all forming two bonds to the underlying surface. First, it could bridge the two Si atoms forming a single dimer ("atop"); second, it could bond between two adjacent dimers in a single dimer row ("bridge-bonded"), or third, it could bond between two adjacent Si atoms in adjacent dimer rows. The STM images in fig. 2 show that features A and B both have maxima directly on top of a Si=Si dimer, and therefore show the symmetry anticipated for an adsorbed PH_3 molecule which has formed two new bonds to a single Si-Si dimer. This presumably takes place by breaking the weak π bond of the Si=Si dimer, and forming two new bonds (one from each Si atom in the dimer) to the adsorbed specie. Based on the symmetry of the STM images, we conclude that PH_3 adsorbs on the Si(001) surface as depicted in fig. 7. This configuration is essentially identical to that proposed by Yu, et al.¹⁶

We consider first whether this is expected to be a stable configuration. During adsorption of PH_3 onto the Si(001) surface, the weak π bond of the Si=Si is dimer is broken and two new Si-P bonds are formed. The length of such a Si-Si single bond should be approximately the same length as the Si-Si bond length in the Si(001)-(2x1)H monohydride structure, which Chabal and Raghavachari²⁷ determined to be 2.51 Å. Although no information could be found on pentacoordinate P-Si compounds, the Si-P bond length in the molecules H_3Si-PH_2 and $P(SiH_3)_3$ are 2.249 and 2.248

Å, respectively.²⁸ Assuming 2.248 Å for the P-Si bond length and 2.51 Å for the Si-Si bond length gives 75.4 degrees for the Si-P-Si bond angle. An examination of the literature on existing pentacoordinate phosphorus compounds fails to show any compounds with formulae such as $H_3P(SiH_3)_2$. However, two general trends are found for 5-coordinate P compounds.²⁶ First, pentacoordinate compounds are stabilized by electronegative substituents, so that compounds such as PF_5 , PHF_4 , and PH_2F_3 are stable, while compounds such as PH_5 are unstable with respect to dissociation to $PH_3 + H_2$. Secondly, although the trigonal bipyramidal structure and square pyramid configurations are preferred for these compounds, distortions from these geometries are readily accommodated in many compounds.

If the adsorption reaction is written as:



the overall thermodynamics can be approximated as:

$$\Delta G = \Delta G(Si=Si \pi \text{ bond}) - 2\Delta G(Si-P); \text{ that is, the overall energy change}$$

is approximately the energy gained by forming two Si-P bonds, minus the energy loss associated by breaking the weak Si=Si π bond.

Although the thermodynamic quantities needed to evaluate the free energy change are unknown, it is not unreasonable to think that this reaction might be quite favorable because of the weakness of the Si-Si dimer π bond. The energy of this bond is variously estimated at 31 kJ/mole,²⁹ 21 kJ/mole,³⁰ and 8 kJ/mole.³¹ The energy of a Si-P bond for phosphorus in a coordination number of 3 is quite large; in the compound SiH_3-PH_2 , for example, the P-Si bond dissociation energy is 88.0 kcal/mole = 368 kJ/mole.³² However, a search of the literature failed to turn up any stable compounds incorporating P-Si bonds with a phosphorus coordination of 5. Based on a rough analysis of the line shape observed in temperature-programmed desorption experiments at high coverage, Yu, et al.^{15,16} obtained an estimated value of 0.6 eV (= 58 kJ/mole) for the activation barrier to PH_3 desorption.

Assuming a simple desorption pathway, this leads to a bond dissociation energy of no more than 58 kJ/mole, for a total energy change on the order of 30 kJ/mole for the adsorption process. The

amount of energy required to remove a Si atom from the bulk and adsorb it on the surface as a free adatom is estimated at approximately 2 eV, or about 200 kJ/mole,³³ which is larger than the overall amount of energy released during the PH₃ adsorption. However, the overall free energy change of the adsorption is expected to be larger at low coverage than at high, and it should be easier to detach Si atoms from existing vacancies than from a "perfect" terrace. Thus, silicon ejection would be expected to be observed mostly at low PH₃ coverage, and ejection would be expected to occur from existing defects more readily than from "perfect" terraces, in agreement with our experimental observations.

We note that the available experimental data on PH₃ adsorption on Si(111) and Si(001) indicates the adsorption on Si(111) is dissociative^{12,14} but on Si(001) is molecular.^{15,16} The increased stability on Si(001) likely arises from differences in the ability of the PH₃ molecule to bond in a coordination number of 5 on Si(001), while achieving similar coordination on Si(111) is more difficult due to the larger distance between adatoms. More subtle effects, such as the ability of the silicon surface to withdraw charge from the PH₃ molecule (which tends to stabilize 5-coordinate P compounds), may also play an important role in the overall stability of the molecular adsorbate.

b) Si ejection

At room temperature, individual Si adatoms are expected to be only marginally stable, with surface diffusion producing nucleation into dimers and subsequently into larger islands. Based on studies of Si nucleation and growth at elevated temperatures, Mo, et al.^{34,35} determined the activation barrier for surface diffusion of Si to be 0.67 ± 0.8 eV, with a pre-exponential factor of $\sim 10^3$ cm²/sec. Based on these measurements, one would expect that at 300 K the Si atoms would move with a hop rate of between approximately 2-10 Å/sec. With these parameters, it is questionable whether Si atoms would be expected to be visible as stable entities in an STM experiment requiring several minutes. However, small errors in the

surface diffusion measurements could easily lead to small hop rates. Alternatively, defects and other inhomogeneities on the surface could act as trap sites for atoms, effectively reducing their rate of diffusion. Indeed, measurements by Mo, et al.³⁵ indicate that surfaces with defects present show larger number of islands, which they attributed to defect "trapping" of diffusing adatoms.

The ejection of silicon onto a Si(001) surface has been previously observed by Cahill and Avouris³⁶ when Si(001) is exposed to molecular oxygen at room temperature. They observed "bright" features approximately 1 Å high both at positive and negative sample bias. While after annealing to form dimers they observed the characteristic splitting of the π^* antibonding state typical of Si=Si dimers (as in our figure 3), they reported that they did *not* observe a similar splitting for the features produced by room temperature exposure without annealing. Although they attributed the species both before and after annealing to Si dimers, we believe that at least some of the species produced after room-temperature exposure to either oxygen or phosphine are in fact individual Si adatoms, not dimers.

In order to compare the features produced by oxygen exposure with those produced by PH₃ exposure, we also conducted experiments in which Si(001) surfaces were exposed at room temperature to oxygen. Figure 8 shows that oxygen exposure produces large depressions and also white protrusions which appear identical in all respects with those observed by Cahill and Avouris. While they were unable to obtain atomic resolution after oxygen exposure, our atomic-resolution images clearly reveal the bonding symmetry of these features. An important result of this experiment is that the protrusions produced by exposure of Si(001) to oxygen and the "A" features produced by exposure to phosphine have *identical* symmetry, with a maximum located directly above a Si=Si dimer. As depicted in figure 7, this bonding location is inconsistent with the identification of these features as Si=Si ad-dimers, but is consistent with their identification as individual Si adatoms. In the STM images, these individual Si adatoms appear as protrusions both at negative and positive bias; this is consistent

with the simple bonding picture in fig. 7, in which each adsorbed Si adatom has two bonds to the substrate and two unsaturated "dangling bonds", which extend into the vacuum and parallel to the dimer rows. The directional nature and spatial extent of these "dangling bonds" results in the oblong shape of the "A" features. We note that oxygen contamination in the phosphine can be ruled out as the source of the ejected adatoms, both because of the purity of the starting material and because of the much lower sticking coefficient of oxygen compared with phosphine.

Conclusions

In agreement with previous studies by Yu and coworkers,^{15,16} we have observed that the adsorption of PH₃ on the Si(001) surface occurs molecularly at room temperature. The adsorption process is accompanied by ejection of silicon atoms from the substrate onto the surface, creating vacancies and Si adatoms. Most of the ejected Si atoms come from existing defect sites due to the lower binding energy of Si atoms at these defects. The PH₃ molecules spontaneously order at room temperature into an ordered c(4x2) configuration whose long-range order is interrupted by domain boundaries and by the ejected silicon, which orders into small dimer strings at high PH₃ coverage. Annealing PH₃-exposed surfaces to temperatures where phosphorus desorbs produces extensive Si atom ejection onto the substrate terrace, indicating that P atoms readily substitute into the Si surface during the decomposition and desorption process.

Acknowledgments

This work was supported in part by the U.S. Office of Naval Research and by the National Science Foundation. M.J.B. wishes to thank the National Science Foundation for a Postdoctoral Research Fellowship in Chemistry.

References

- (1)Eversteyn, F.; Put, B. H. *J. Electrochem. Soc.* **1973**, *120*, 106-110.
- (2)Chang, C. A. *J. Electrochem. Soc.* **1976**, *123*, 1245-1247.
- (3)Kurokawa, H. *J. Electrochem. Soc.* **1982**, *129*, 2620-2624.
- (4)Meyerson, B. S.; Olbricht, W. *J. Electrochem. Soc.* **1984**, *131*, 2361-2365.
- (5)McCarthy, M. J.; Meyerson, B. S.; Reimer, J. A. *J. Appl. Phys.* **1987**, *62*, 3665-3670.
- (6)Madsen, L. D.; Weaver, L. *J. Electrochem. Soc.* **1990**, *137*, 2246-2251.
- (7)Wang, W.-C.; Denton, J. P.; Neudeck, G. W. *J. Vac. Sci. Technol. B* **1993**, *11*, 117-119.
- (8)Grundmann, M.; Krost, A.; Bimberg, D. *Appl. Phys. Lett.* **1991**, *58*, 284-286.
- (9)Meyerson, B. S.; Yu, M. L. *J. Electrochem. Soc.* **1984**, *131*, 2366-2366.
- (10)van Bommel, A. J.; Crombeen, J. E. *Surf. Sci.* **1973**, *36*, 773-777.
- (11)Bozso, F.; Avouris, P. *Phys. Rev. B* **1991**, *43*, 1847 - 1850.
- (12)Wallace, R. M.; Taylor, P. A.; Choyke, W. J.; Yates, J. T., Jr. *J. Appl. Phys.* **1990**, *68*, 3669-3678.
- (13)Taylor, P. A.; Wallace, R. M.; Choyke, W. J.; Yates, J. T., Jr. *Surf. Sci.* **1990**, *238*, 1 - 12.
- (14)Chen, P. J.; Colaianni, M. L.; Wallace, R. M.; Yates, J. T., Jr. *Surf. Sci.* **1991**, *244*, 177-184.
- (15)Yu, M. L.; Meyerson, B. S. *J. Vac. Sci. Technol. A* **1984**, *2*, 446-449.
- (16)Yu, M. L.; Vitkavage, D. J.; Meyerson, B. S. *J. Appl. Phys.* **1986**, *59*, 4032-4037.
- (17)Hamers, R. J.; Tromp, R. M.; Demuth, J. E. *Phys. Rev. B* **1986**, *34*, 5343 - 5357.
- (18)Hamers, R. J.; Köhler, U. K. *J. Vac. Sci. Technol. A* **1989**, *7*, 2854-2859.
- (19)Boland, J. J. *J. Vac. Sci. Technol. A* **1992**, *10*, 2458-2464.
- (20)Wang, Y.; Bronikowski, M. J.; Hamers, R. J. *J. Vac. Sci. Tech. A* **1993**, in press.
- (21)Hamers, R. J.; Tromp, R. M.; Demuth, J. E. *Surf. Sci.* **1987**, *181*, 246 - 355.

- (22) Bronikowski, M. J.; Wang, Y.; McEllistrem, M. T.; Chen, D.; Hamers, R. J. *Surf. Sci.* **1994**, *298*, 50-62.
- (23) Wang, Y.; Chen, X.; Hamers, R. J. *Surf. Sci.* **1994**, (submitted).
- (24) Tromp, R. M.; Denier van der Gon, A. w.; Reuter, M. C. *Phys. Rev. Lett.* **1992**, *68*, 2313-2316.
- (25) Wang, Y.; Bronikowski, M. J.; Hamers, R. J. *Surf. Sci.* **1993**, *In press*.
- (26) Holmes, R. R. *Pentacoordinated Phosphorus, Vol. I and II*; American Chemical Society: Washington, D.C., 1980.
- (27) Chabal, Y. J.; Raghavachari, K. *Phys. Rev. Lett.* **1984**, *53*, 282.
- (28) Ayllett, B. J. In *Advances in Inorganic Chemistry and Radiochemistry*; J. J. Emeleus and A. G. Sharpe, Eds. 1986; Vol. 11; pp 249.
- (29) D'Evelyn, M. P.; Yang, Y. L.; Sutcu, L. F. *J. Chem. Phys.* **1992**, *96*, 852-855.
- (30) Nachtigall, P.; Jordan, K. D.; Janda, K. C. *J. Chem. Phys.* **1991**, *95*, 8652.
- (31) Wu, C. J.; Carter, E. A. *Chem. Phys. Lett.* **1991**, *185*, 172-177.
- (32) Saalfeld, F. E.; Svec, H. J. *Inorganic Chem.* **1964**, *3*, 1442-1443.
- (33) Zhang, Z.; Metiu, H. *Phys. Rev. B* **1993**, *48*, 8166-8171.
- (34) Mo, Y. W.; Kleiner, J.; Webb, M. B.; Lagally, M. G. *Surf. Sci.* **1992**, *268*, 275-295.
- (35) Mo, Y. W.; Kleiner, J.; Webb, M. B.; Lagally, M. G. *Phys. Rev. Lett.* **1991**, *66*, 1998.
- (36) Cahill, D. G.; Avouris, P. *Appl. Phys. Lett.* **1992**, *60*, 326-328.

Figure Captions:

- 1a) STM image of Si(001) surface before exposure to PH₃. Dimensions 336 Å x 263 Å; V_{sample} = -2.0 V, I_{tunnel} = 0.3 nA.
- b) STM image of the same region, after exposure to PH₃, showing the appearance of white protrusions and the enlargement of vacancy defects.
- 2a) High-resolution STM image of Si(001) surface exposed to 0.04 L PH₃ at 300 Kelvin, then imaged at V_{sample} = -2.8 V, I_{tunnel} = 0.2 nA; dimensions 106 Å x 106 Å.
- b) Height profiles measured across "A" and "B" features along the lines indicated in fig. 2a, showing the different width, and depicting the overall symmetry of these features with respect to the underlying Si lattice.
- c) High-resolution STM image of PH₃-exposed surface, with lines showing that features "A" and "B" are both maximized at a position directly above a Si=Si dimer. V_{sample} = -2.0 V, I_{tunnel} = 0.2 nA; dimensions 58 Å x 49 Å.
- d) STM image of same area as (c) at positive bias, showing that "A" features remain as protrusions but "B" features now appear as depressions. Imaging conditions V_{sample} = +2.0 V, I_{tunnel} = 0.3 nA.
- 3) STM images of surfaces prepared by exposure to PH₃ at 300 K, then annealing to 500 K for 30 seconds, then cooled to 300 K. Arrows point to locations of dimers ("D") and a dimer string ("DS"). Other features are dissociation fragments and other species.
- a) probing filled surface states, V_{sample} = -2.5 V, I_{tunnel} = 0.2 nA; dimensions 109 Å x 80 Å
- b) same area as a), probing empty surface states, V_{sample} = +2.3 V, I_{tunnel} = 0.03 nA. Note the characteristic splitting of the dimers observed at positive bias.
- c) High-resolution image showing Si=Si dimer strings after annealing, V_{sample} = -2.0 V, I_{tunnel} = 0.2 nA; dimensions 29 Å x 25 Å.

d) High-resolution image of same area as (c), showing apparent splitting of dimers due to nodal structure of π^* antibonding orbital; $V_{\text{sample}} = +2.3\text{ V}$, $I_{\text{tunnel}} = 0.03\text{ nA}$.

in the same configuration as depicted in fig. 7. $V_{\text{sample}} = -1.68\text{ V}$, $I_{\text{tunnel}} = 0.5\text{ nA}$; dimensions $88\text{ \AA} \times 88\text{ \AA}$.

4) STM images obtained after exposure of Si(001) surface to 0.6 L PH_3 at 300 Kelvin .

a) High-resolution image showing ordering of adsorbates onto every second dimer along a dimer row, with a $7.7\text{ \AA}$ period. $V_{\text{sample}} = -2.4\text{ V}$, $I_{\text{tunnel}} = 0.3\text{ nA}$; dimensions $139\text{ \AA} \times 70\text{ \AA}$.

b) Larger area image, showing initial formation of $c(4 \times 2)$ regions. $V_{\text{sample}} = -2.75\text{ V}$, $I_{\text{tunnel}} = 0.3\text{ nA}$; Dimensions $395\text{ \AA} \times 278\text{ \AA}$.

c) Schematic illustration of $c(4 \times 2)$ ordering of adsorbates.

5) Large-scale STM image obtained after saturation exposure of Si(001) surface to PH_3 , showing regions of $c(4 \times 2)$ symmetry and small regions of Si=Si dimer strings produced from ejected Si. Arrows point to regions of PH_3 ordered in $c(4 \times 2)$ symmetry.

$V_{\text{sample}} = -2.0\text{ V}$, $I_{\text{tunnel}} = 0.16\text{ nA}$; dimensions $491\text{ \AA} \times 491\text{ \AA}$.

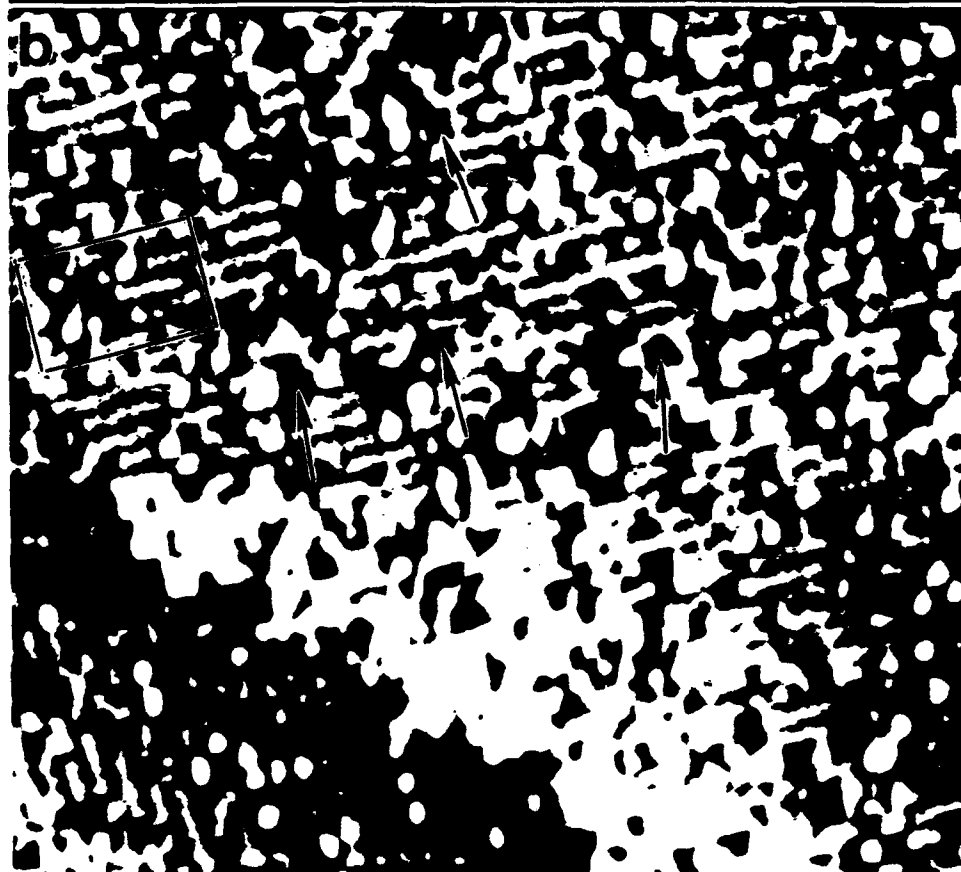
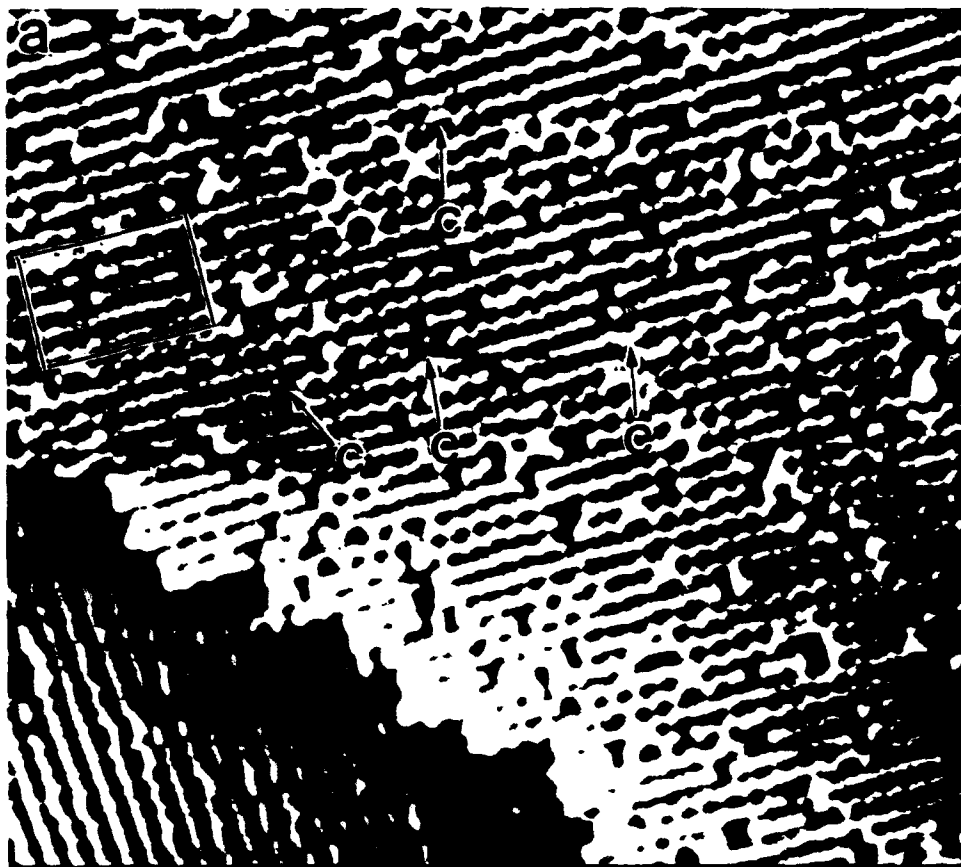
b) High-resolution image showing small domains of PH_3 molecules adsorbed in $c(4 \times 2)$ symmetry (arrows). $V_{\text{sample}} = -2.0\text{ V}$, $I_{\text{tunnel}} = 0.15\text{ nA}$; dimensions $126\text{ \AA} \times 126\text{ \AA}$.

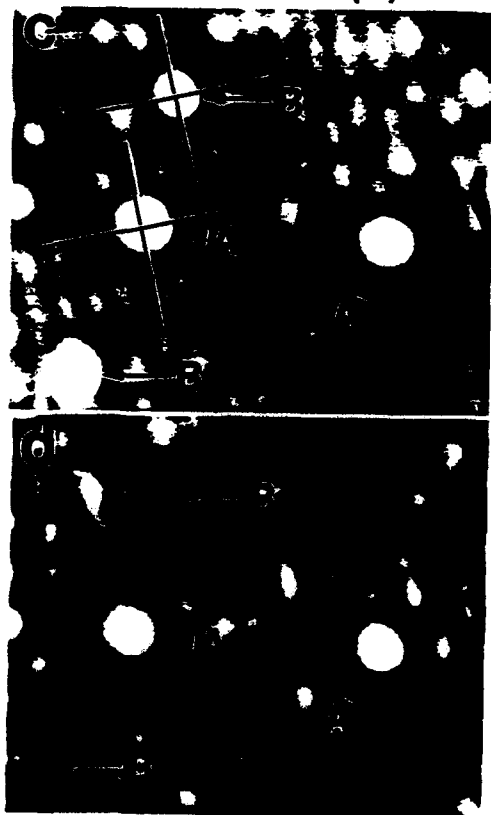
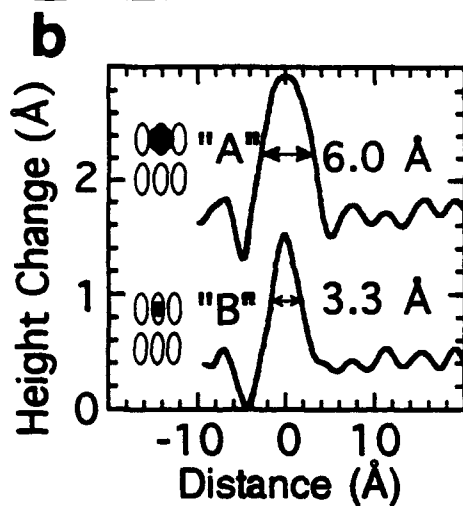
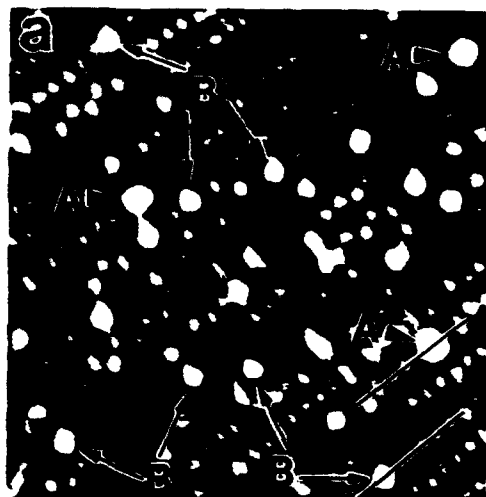
c) High-resolution image showing small regions with Si=Si dimer strings (arrows). $V_{\text{sample}} = -2.0\text{ V}$, $I_{\text{tunnel}} = 0.16\text{ nA}$; dimensions $189\text{ \AA} \times 189\text{ \AA}$.

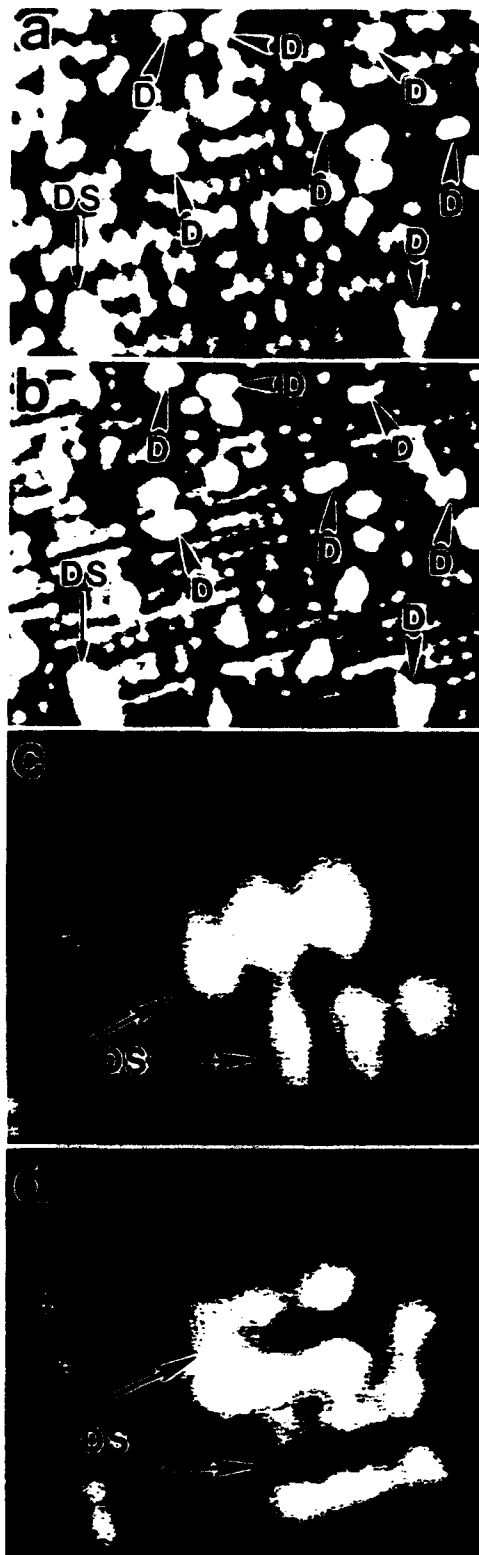
6) STM image of surface exposed to saturation coverage of PH_3 at 300 Kelvin , then annealed to 950 Kelvin . The islands occupy 20% of the surface area when measured away from step edges. $V_{\text{sample}} = -2.0\text{ V}$, $I_{\text{tunnel}} = 0.2\text{ nA}$; dimensions $2400\text{ \AA} \times 2400\text{ \AA}$.

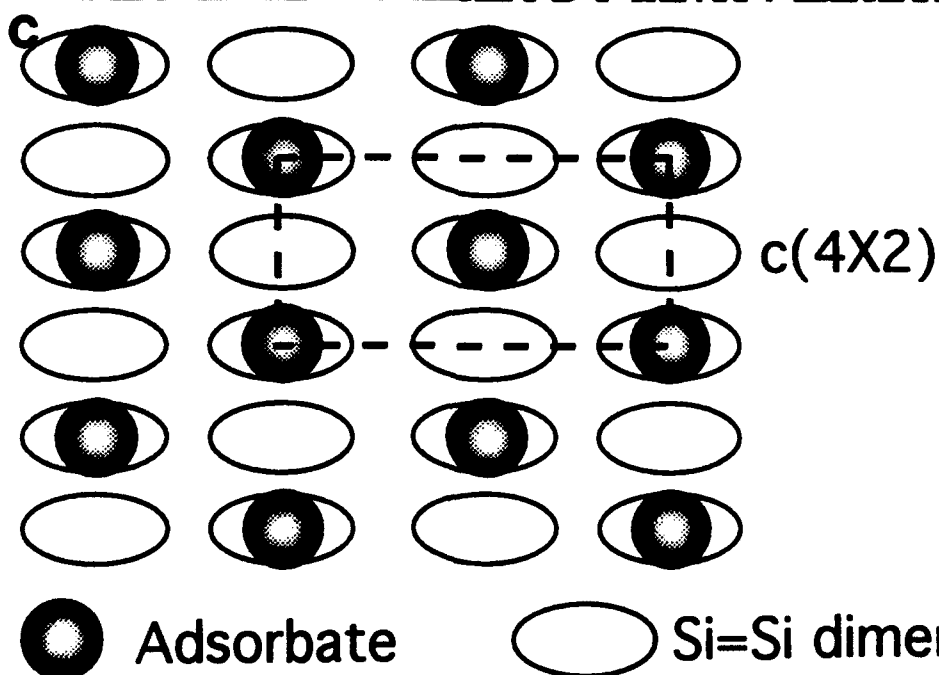
7) Models depicting adsorption locations of molecularly-adsorbed PH_3 group, adsorbed silicon adatom, and Si=Si ad-dimer in "atop" configuration on Si(001) surface.

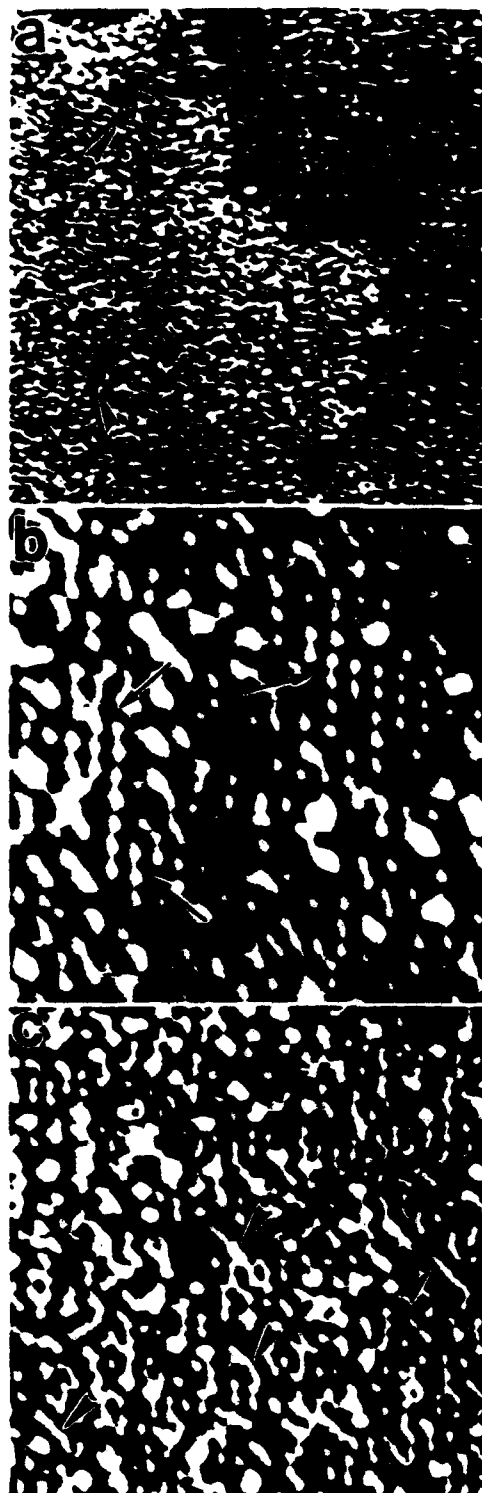
8) STM image of Si(001) surface exposed to 1 Langmuir oxygen, showing ejected silicon atoms bonded directly above a single adatom





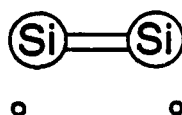
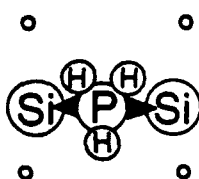
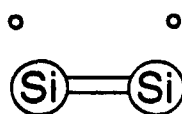
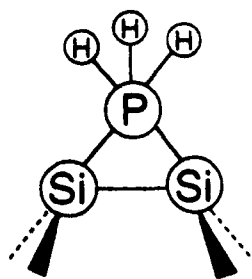




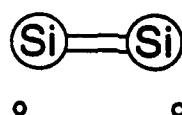
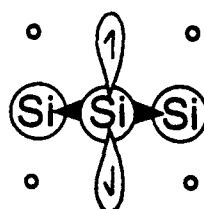
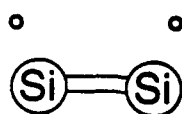
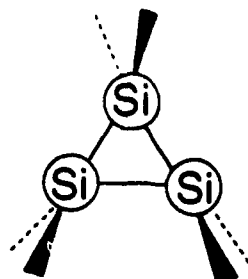




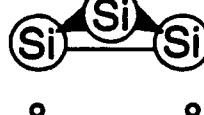
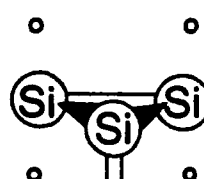
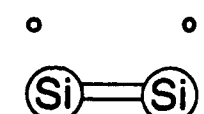
Wang et al.
Fig. 6



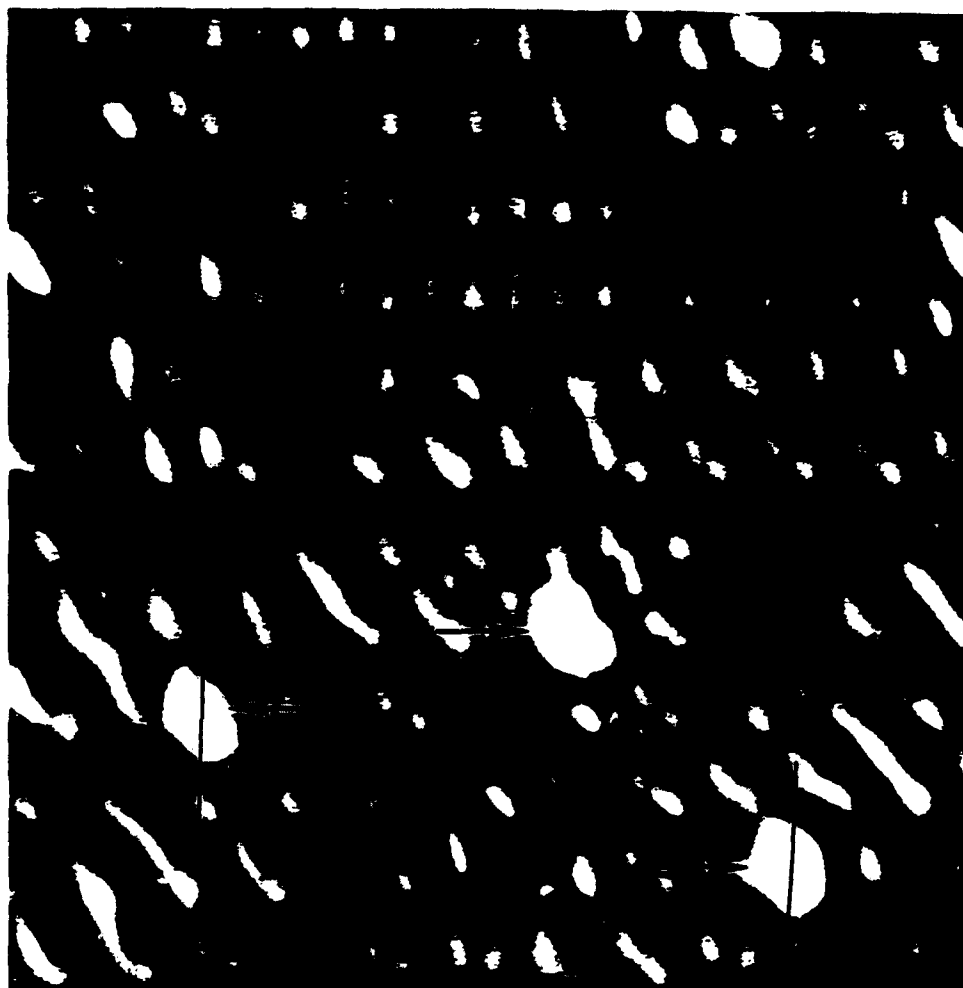
Molecular
 PH_3



Si
Adatom



Si
Ad-dimer



Wang et al
Fig. 8