Phosphine Dissociation and Diffusion on Si(001) Observed at the Atomic Scale

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A detailed atomic-resolution scanning tunneling microscopy (STM) and density functional theory study of the adsorption, dissociation, and surface diffusion of phosphine (PH₃) on Si(001) is presented. Adsorbate coverages from ~0.01 monolayer to saturation are investigated, and adsorption is performed at room temperature and 120 K. It is shown that PH₃ dissociates upon adsorption to Si(001) at room temperature to produce both PH₂ + H and PH + 2H. These appear in atomic-resolution STM images as features asymmetric-about and centered-upon the dimer rows, respectively. The ratio of PH₂ to PH is a function of both dose rate and temperature, and the dissociation of PH₂ to PH occurs on a time scale of minutes at room temperature. Time-resolved in situ STM observations of these adsorbates show the surface diffusion of PH₂ adsorbates (mediated by its lone pair electrons) and the dissociation of PH₂ to PH. The surface diffusion of PH₂ results in the formation of hemihydride dimers on low-dosed Si(001) surfaces and the ordering of PH molecules along dimer rows at saturation coverages. The observations presented here have important implications for the fabrication of atomic-scale P dopant structures in Si, and the methodology is applicable to other emerging areas of nanotechnology, such as molecular electronics, where unambiguous molecular identification using STM is necessary.

1. Introduction

The ability to controllably position P dopant atoms into Si at the nanoscale is currently being developed by several groups because of the potential for creating nanoelectronic devices such as silicon single-electron transistors and quantum cellular automata. This becomes particularly interesting when the control is extended to the level of positioning individual P dopant atoms, which leads to the possibility of creating novel devices such as a single-dopant transistor or even a silicon-based quantum computer. One promising method for achieving such atomic-scale control over the position of individual P atoms in Si is by controlling the chemical reaction of phosphine (PH₃) molecules with the Si(001) surface by using scanning tunneling microscopy (STM). The interaction of PH₃ with the Si(001) surface has been the subject of numerous publications over the last two decades, using a variety of surface science techniques such as high-resolution electron energy loss spectroscopy (HREELS), temperature programmed desorption (TPD), Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), density functional theory calculations (DFT), and scanning tunneling microscopy (STM). In one of the earliest studies, Colaianni et al. used HREELS and TPD to show that PH₃ adsorbs dissociatively at room temperature with no evidence for molecularly adsorbed PH₂. Subsequent FTIR and XPS measurements conclusively demonstrated that there are at least two major adsorbate species on Si(001) after exposure to PH₃ gas and that the relative concentration of these two species varies as a function of PH₃ dosing rate and substrate temperature. Despite the earlier report of dissociative adsorption by Colaianni et al., they interpreted their FTIR data as evidence for both PH₃ and PH₂ adsorbates, and this interpretation was adopted by Lin and co-workers in their XPS study. Atomic-resolution STM studies by three separate groups did little to clarify the adsorption process. These studies reported that PH₃ adsorption to Si(001) results in primarily a single adsorbate species that appears in STM images as a circular (sometimes slightly elongated) protrusion located symmetrically above the Si dimers. This adsorbate was respectively assigned to molecularly adsorbed PH₃, dimer-inserted PH₂, and surface P–P ad-dimers. However, the possibility of this adsorbate being PH₃ was conclusively ruled out by DFT calculations performed by several different groups, which showed that PH₃ could only adsorb to Si(001) in the dangling-bond position, and even then was unstable with respect to dissociation to PH₂. In addition, both dimer-inserted PH₂ and surface P–P are unlikely due to energetic barrier considerations. A less abundant feature seen in the STM images (that is also symmetric about the dimer rows) was assigned to etched Si monomers, similar to the initial assignment of etched Si monomers by Wang et al.

In an attempt to clarify the adsorption of PH₃ to Si(001) and, in particular, to understand STM images of this surface, we have embarked on an extensive investigation of this system by combining atomic-resolution STM measurements and DFT calculations. We have recently reported that the centered,
circular adsorbate seen in previous STM studies is PH bonded in a bridge-site position above a Si dimer, with the two dissociated H atoms adsorbed to the adjacent Si dimer.21,22 We have also reported the identification of several additional PH-related adsorbate species in STM images,21,22 by far the most common of which produces a feature that is asymmetric about the dimer rows in STM images and which we believe is PH and H bonded to opposite sides of a single Si dimer.

Our previous reports21,22 have presented detailed DFT calculations of the adsorption and dissociation of PH3 on Si(001), including total energy as well as barrier calculations, and discussed the expected surface features based on both thermodynamic and kinetic reaction considerations. Here, we present the direct experimental observation of PH2 dissociation and diffusion on Si(001) in a detailed experimental atomic-resolution STM study. In particular, we conclusively demonstrate that the PH + 2H feature (centered protrusion) results from the surface dissociation of PH3 from the PH3 + H feature (asymmetric protrusion) to PH and a monohydride dimer. This dissociation process takes place on a time scale of minutes (in agreement with FTIR and XPS data11-14), and so the relative concentration of PH2 and PH on saturation-dosed surfaces can be controlled by varying the dose rate. We show that the dissociation of PH3 to PH does not occur at low temperature (120 K), but begins to occur upon warming the substrate to 200 K, in qualitative agreement with an Arrhenius temperature dependence. In addition, we show that at low surface-coverage PH3 is able to diffuse on the Si(001) surface parallel to the dimer rows. This diffusion is closely related to the mechanism by which PH2 dissociates to PH. We show that the surface diffusion of PH2 is responsible for the formation of isolated hemihydride dimers on Si(001) after PH2 dosing; this hemihydride dimer formation was previously a mystery, as it is known that H atoms do not surface diffuse on Si(001) at room temperature.23 Finally, we show that the kinetics of PH2 diffusion is responsible for the formation of ordered regions of PH + 2H molecules on Si(001) at high surface coverage.

The in situ experimental observations presented here are in excellent agreement with extensive DFT calculations21,22 and together present a coherent picture for a complete mechanism of PH3 adsorption and subsequent dissociation and diffusion on Si(001). This picture also fits well with the available data in the literature, with the slight concession that the interpretation of PH3 and PH2 adsorbates in a small number of publications should be reinterpreted as PH2 and PH, and we discuss good reasons for doing this at the end of the paper.

2. Experimental Section

Experiments were performed by using an Omicron variable temperature STM inside an ultrahigh vacuum (UHV) chamber with base pressure <5 × 10^-11 mbar. Phosphorus-doped 10^15 cm^-3 wafers, oriented toward the [001] direction, were used. All Si samples were handled only by using ceramic tweezers and mounted in tantalum/molybdenum/ceramic sample holders to avoid contamination. Sample preparation was performed by outgassing overnight at 850 K, followed by oxide removal at 1400 K and cooling slowly (∼3 K/s) from 1150 K to room temperature.24 PH3 is a dangerous gas, being both highly toxic and flammable, and so special care was taken in its use in our laboratory: less than one cubic centimeter of ultrapure PH3 gas at atmospheric pressure was housed in a leak-monitored double-walled containment system. PH3 was admitted to the STM chamber via a leak valve with line-of-sight to the sample while mounted in the STM. Care was taken to ensure no hot filaments were close by or in line-of-sight to the sample during PH3 dosing to ensure that the PH3 was not dissociated before reaching the sample surface.

3. Saturation-Dosed Surfaces

A useful way to observe the bonding arrangements of molecules on Si(001) is to limit the spatial extent of the adsorption to only a small area by using hydrogen lithography.25,26 This is achieved by terminating the surface with a monolayer of hydrogen and subsequently removing the H from a small region by performing electron stimulated desorption using the highly confined electron beam of the STM tip. An example of this is shown in Figure 1A, where a ∼300 × 50 nm^2 rectangular patch of bare Si(001) surface has been exposed on an otherwise H-terminated Si(001) surface (details of the H termination and H lithography steps have been presented previously). The patch of bare Si(001) surface appears brighter in the STM image due to the additional STM tunneling current that arises from the Si surface π-states.27 The surface shown in Figure 1A was subsequently exposed to 0.14 L of PH3 at a chamber pressure of 1 × 10^-9 mbar, and a small section of the PH3 dose surface is shown in Figure 1B. The PH3 molecules are not able to adsorb on the chemically passivated areas of H-terminated surface that surround this patch, which can therefore be used as a reference where the (2 × 1) dimer periodicity of the Si(001) surface can be observed. This allows the identification of the bonding sites and surface ordering of the adsorbates within the patch with respect to the Si(001) surface.

Both the PH + 2H and PH2 + H features are seen within the lithographic patch in Figure 1B. Four of the PH + 2H features are shown in Figure 1C, which is an enlargement of the top left corner of Figure 1B. These molecules are adsorbed on every other dimer along the dimer row, consistent with first principles calculations that predict the formation of a monohydride dimer adjacent to the PH molecule.21,22 Figure 1D shows an enlargement of the bottom right corner of Figure 1B, where four of the PH2 + H features can be observed. We see from Figure 1B and D that these molecules self-order on the surface.
with a \( p(2 \times 2) \) periodicity. The schematic shown in Figure 1E shows the bonding locations and ordering for the four \( \text{PH} + 2\text{H} \) and four \( \text{PH}_2 + \text{H} \) features shown in Figure 1C and D, respectively. The majority of features within the lithographic patch can be attributed to \( \text{PH}_2 + \text{H} \) or \( \text{PH} + 2\text{H} \) features; however, a small number of depression and protrusion features can be attributed to isolated H atoms and Si dangling bonds. The observation of these adsorbates and, in particular, their self-ordering on the surface, confirms these as the primary \( \text{PH}_x \) \( (x = 1, 2) \) moieties formed after dosing the Si(001) surface to saturation coverage at room temperature.

Changes in the ratio of \( \text{PH}_2 \) to \( \text{PH} \) are observed to occur during the course of an STM experiment. This suggests that the dissociation from \( \text{PH}_2 \) to \( \text{PH} \) may take place on a time scale of minutes. If this is so, a sample that is dosed very slowly, i.e., over a period of some hours, should exhibit an elevated number of \( \text{PH} + 2\text{H} \) features compared to that of a surface dosed to saturation more quickly, and we have found that this is indeed the case. Figure 2A shows a surface dosed to saturation in \( \sim 10 \) min by filling the chamber to a pressure of \( 1 \times 10^{-9} \) mbar. This surface has a high number of \( \text{PH}_2 + \text{H} \) features and patches of these molecules ordering with \( p(2 \times 2) \) periodicity can be seen, as highlighted by the white arrow.

The surface shown in Figure 2B was formed by dosing with a \( 3 \times 10^{-11} \) mbar partial pressure of \( \text{PH}_3 \) and dosing for 100 minutes. As expected, the number of \( \text{PH} + 2\text{H} \) features has increased compared to that of the surface in Figure 2A. In addition, we see a tendency for the \( \text{PH} \) molecules to line up along a dimer row (due to the anisotropic diffusion of \( \text{PH}_2 \) that we will discuss below), and in all cases, the centered protrusions are separated by at least one dimer width. Nevertheless, small patches of \( \text{PH}_2 \) features with \( p(2 \times 2) \) periodicity can be observed on this surface. Finally, we have dosed a Si(001) sample at the slowest rate possible in our instrument by dosing the sample for 5 h with the total chamber pressure raised by just \( 1 \times 10^{-11} \) mbar above background pressure. The resulting surface, shown in Figure 2C, exhibits an even greater proportion of \( \text{PH} + 2\text{H} \) features (over 200 in Figure 2C compared with \( \sim 150 \) in Figure 2B), with only a few small regions of \( \text{PH}_2 + \text{H} \) observable in the image (Note that in each case these images are representative of the entire surface of the sample). Figure 2 represents direct experimental evidence that the \( \text{PH} + 2\text{H} \) feature (centered protrusion) is the dissociation product of \( \text{PH}_2 \) from the \( \text{PH}_2 + \text{H} \) feature (asymmetric protrusion). Furthermore, these images unambiguously demonstrate that this dissociation takes place on a time scale of minutes at room temperature and occurs regardless of whether the surface is imaged with the STM or not.

### 4. Adsorption at Low Temperature

The dissociation of \( \text{PH}_3 \) on Si(001) is an activated process that is expected to follow an Arrhenius dependence on temperature. Therefore, the dissociation should be inhibited when the sample is cooled to cryogenic temperatures. Figure 3 shows the results of two experiments where the \( \text{PH}_3 \) dosing and STM imaging were performed at cryogenic temperature by coupling the sample to a liquid nitrogen cryostat. The sample temperature was monitored by a silicon diode coupled to the sample holder. The surface shown in Figure 3A was cooled to \( \sim 120 \) K and then exposed to 0.008 L of \( \text{PH}_3 \) at a chamber pressure of \( 3 \times 10^{-11} \) mbar. This surface exhibits a uniform coverage of \( \text{PH}_2 + \text{H} \) features, but has a complete absence of any \( \text{PH} + 2\text{H} \) features. The surface shown in Figure 3A was imaged continuously for several hours with no observation of \( \text{PH} + 2\text{H} \) features. We have also dosed Si(001) samples to saturation coverage with \( \text{PH}_3 \) at 120 K (not shown) and, again, find no evidence for any \( \text{PH} + 2\text{H} \) features. The absence of \( \text{PH} + 2\text{H} \) features is consistent with the dissociation of \( \text{PH}_3 \) to \( \text{PH} \) being inhibited at 120 K and further confirms our assignment of the centered feature to \( \text{PH} \) molecules resulting from the dissociation of \( \text{PH}_2 \) on the surface.
A closer inspection of Figure 3A reveals that there appear to be two distinct types of asymmetric features, as indicated by the white and black arrows, respectively. This second asymmetric protrusion can reasonably be attributed to molecularly adsorbed PH$_3$ molecules because the dissociation of PH$_3$ to PH$_2$ may be inhibited at 120 K to the point where some undissociated PH$_3$ remains on the surface.

Alternatively, these features may be attributed to a different configuration of PH$_2$, for example, one in which the dimer end opposite to the PH$_2$ is not terminated with a H atom. We will discuss further below how such structures may come about. Further low-temperature experiments are underway to rule out one or another of the above possibilities and identify the second asymmetric protrusion seen at 120 K as either undissociated PH$_3$ or an alternate configuration of PH$_2$.

Figure 3C shows a Si(001) surface exposed to PH$_3$ at 120 K and then allowed to warm slightly to 200 K. In this image, several PH + 2H features can be seen, indicating that some dissociation of PH$_2$ to PH occurs at this temperature. The relatively low coverage of PH + 2H features in Figure 3C compared to that of a surface exposed to an equal fluence of PH$_3$ at room temperature is consistent with an Arrhenius temperature dependence for PH$_2$ dissociation.

5. Quantum Chemistry Calculations

To further understand the dissociation processes leading from molecularly adsorbed PH$_3$ to PH$_2$ + H and PH + 2H species, we have conducted quantum chemical calculations of the energetics of these species and explored probable reaction pathways and transition barriers. The objective of these calculations is to provide an overview of the activation energies that govern the observed transitions. We present here only the key aspects of our theoretical results relative to the observed transitions, and refer the reader to the full details to be published elsewhere. Briefly, our calculations were conducted at the B3LYP/6-311++G(d,p) level of density functional theory (DFT) using a three-dimer Si$_2$H$_2$ cluster model of the Si(001) surface. We note that this type of cluster model has been widely used in the literature to describe reactions on the Si(001) surface and has been found to give adequate reaction energies. In our calculations, all atomic positions are fully relaxed with the exception of the cluster terminating H atoms, which are locked into position along truncated Si–Si bonds so as to mimic the strain imposed on the cluster by the surrounding crystal. We note further that, for computational efficiency, the atomic basis set is truncated for second-layer Si atoms to the 6-311G(d) level and for third- and fourth-layer Si atoms as well as the cluster-terminating H atoms to the LANL2DZ level. All calculations were conducted using the Gaussian 03 software.

An overview of our computational results is shown in Figure 4. For clarity and consistency, we adopt the nomenclature of ref 22 (Warschkow et al., 2005) where PH$_x$ + (3 - $x$)H structures with $x = 3$, 2, and 1 are designated by using the letters A, B, and C, respectively, and different bonding geometries are sequentially numbered. In particular, we designate molecularly adsorbed PH$_3$ as structure A1, three different configurations of PH$_2$ + H as structures B1, B2, and B4, and PH + 2H as structure C1 (see Figure 4A).

A schematic of two reaction pathways from adsorbed PH$_3$ to PH$_2$ + 2H (A1 $\rightarrow$ B1 $\rightarrow$ B4 $\rightarrow$ C1 and A1 $\rightarrow$ B2 $\rightarrow$ B4 $\rightarrow$ C1) is shown in Figure 4A. The corresponding energetics of the intermediate structures and transition states are shown in Figure 4B. The dissociation of molecularly adsorbed PH$_3$ (A1) to PH$_2$ + H, with both fragments attached to opposite ends of the same dimer (B1), has been described previously by Miotto et al. In qualitative agreement with these calculations, we find that the formation of B1 leads to a substantial stabilization of 1.40 eV and is accessible with a relatively low activation energy of 0.76 eV (Figure 4B). An alternative dissociation channel is one that leads to structure B2 (Figure 4A) via a proton-shift reaction to an adjacent dimer in a manner analogous to that reported for NH$_3$ dissociation on Si(001) by Smedarchina et al. The activation barrier for the dissociation from PH$_3$ (A1) to structure B2 is 0.54 eV, which is 0.22 eV lower than the barrier for dissociation from PH$_3$ to structure B1. Thus, B2 is the kinetically favored product, and we therefore expect some of the molecularly adsorbed PH$_3$ to dissociate via the B2 structure. Structure B1, however, is 0.50 eV more stable than B2 and is therefore the thermodynamically favored product.

We now consider the further dissociation of products B1 and B2 toward the PH + 2H feature, C1. In structure C1, PH is centered on top of a Si–Si dimer, forming a three-membered ring, and the two hydrogen atoms are attached to a neighboring dimer in the same row. We identify structure B4 as the most likely, if highly transient, precursor to C1. As shown in Figure 4, the B4 structure contains a dimer centered PH$_2$ and a H atom on the adjacent dimer. Both the B1 $\rightarrow$ B4 and B2 $\rightarrow$ B4 reactions are endothermic. B4 is 0.98 eV less stable than B1 and 0.48 eV less stable than B2, which makes B4 a very short-lived (transient) intermediate; once formed, it will either quickly convert to the much more stable PH + 2H structure C1 (irreversible) or else convert back to one of the PH$_2$ + H structures B1 and B2.
Structure B4 is reached from structure B2 by a one-step reaction in which the lone pair on the phosphorus extends to the free Si atom on the other dimer end. This leads to the formation of a second bond between P and Si, which closes the three-membered ring. The path from B1 to B4 is more complicated and involves several steps; principally, a shift of the \( \text{PH}_2 \) group from one Si–Si dimer end to the next, followed by a ring-closure reaction to form structure B4 with \( \text{PH}_2 \) in the dimer-center position. It is the second step, the ring-closure, that has the highest energy and is therefore the rate-determining transition state in the formation of B4.

From the calculated transition barriers, the (classical) rate of dissociation can be estimated via an Arrhenius ansatz and a typical attempt frequency of \( 10^{14} \text{ s}^{-1} \). This yields a room-temperature lifetime below 0.1 s for the dissociation of molecularly adsorbed \( \text{PH}_3 \) (structure A1) to both \( \text{PH}_2 + \text{H} \) structures B1 and B2 (the barriers are 0.76 and 0.54 eV, respectively). This is consistent with the nonobservation of undissociated \( \text{PH}_3 \) on Si(001) at room temperature in our STM measurements.

The lifetime of the thermodynamically favored \( \text{PH}_2 + \text{H} \) structure B1 (the asymmetric feature in STM images) is dependent on the highest transition point along a low-energy reaction path, leading to the more stable \( \text{PH} + 2\text{H} \) structure C1. This highest transition point (given by the B4–C1 reaction step) yields an effective barrier of 1.31 eV, which B1 has to surmount before it can stabilize to C1. Thus, the reaction of the B1 \( \text{PH}_2 + \text{H} \) structure to the \( \text{PH} + 2\text{H} \) feature C1 will occur much more slowly than the dissociation of molecularly adsorbed \( \text{PH}_3 \) to \( \text{PH}_2 + \text{H} \). This is in good qualitative agreement with our STM observation of a mixture of \( \text{PH}_2 + \text{H} \) and \( \text{PH} + 2\text{H} \) on Si(001) at room temperature and a complete absence of any undissociated \( \text{PH}_3 \). We note that the calculated barrier height of 1.31 eV for the B1–C1 transition is slightly too high for the experimentally observed rate of the order of minutes (suggesting a barrier of \( \sim 1.1 \text{ eV} \)); however, this is within the expected errors associated with making quantitative predictions from such calculations. In particular, we note that the crucial B4–C1 transition is a proton-shift reaction and that consideration of quantum tunneling effects can lead to a substantial enhancement of the expected rate of such reactions. The kinetically favored \( \text{PH}_2 + \text{H} \) structure B2 can stabilize to either the \( \text{PH} + 2\text{H} \) (asymmetric feature; structure B1) or to \( \text{PH} + 2\text{H} \) (centered feature; structure C1) with effective barriers of 0.67 and 0.80 eV, respectively. These barriers are only marginally higher than A1–B1/B2 transitions. Thus, while the B2 structure is the kinetically favored dissociation product of molecularly adsorbed \( \text{PH}_3 \) (A1), it dissociates to C1 or rearranges to B1 almost as rapidly as it is formed. This explains the absence of any features in our room-temperature STM experiments that are consistent with the B2 structure.

### 6. Surface Diffusion

We now turn our attention to imaging individual, isolated \( \text{PH}_x \) (\( x = 1, 2 \)) adsorbates at room temperature on lightly \( \text{PH}_3 \)-dosed Si(001) surfaces and compare successive images of the same area to observe dissociation and/or diffusion events. To do this, it is necessary to observe a large enough area that both the initial and final positions of the molecule can be determined (the scan speed of the STM is much slower than the time it takes for individual events to occur). In most cases, on the Si(001) surface, it is sufficient to observe a region of surface bounded by two neighboring step edges. Figure 5 shows a series of filled-state STM images that have been cropped down from larger (50 x 50 nm²) images (not shown), where two such neighboring step edges are visible. In Figure 5A, we see a \( \text{PH}_2 + \text{H} \) feature (top right arrow), with a hemihydride dimer on the adjacent row (bottom left arrow).

The hemihydride dimer in this image exhibits the zigzag appearance known to be characteristic of these features in filled-state STM images. The images shown in Figure 5B–D show the same area of the surface taken in subsequent scans with the STM; the scanning speed of the STM was such that one full image was acquired every 3 min. Careful observation of Figure 5B reveals that the asymmetric feature and the hemihydride dimers have apparently switched places. In fact, it is only the \( \text{PH}_2 \) molecule that moves; this molecule is able to diffuse down the dimer row toward the hemihydride in the adjacent row. At this point, the dangling bond of the hemihydride dimer on the neighboring dimer row presents a low-energy position and the \( \text{PH}_2 \) molecule jumps across the dimer row to occupy this position. The net result is that the hemihydride dimer in Figure 5A is effectively converted into an \( \text{PH}_2 + \text{H} \) feature, while the \( \text{PH}_2 + \text{H} \) feature in Figure 5A is converted to a hemihydride dimer. It should be noted that the conversion of these two features was the only event that occurred along the entire lengths of these two dimer rows between these two images, ruling out the possibility of other molecules on the surface taking part in the transition observed between Figure 5A and B.

The two features discussed in Figure 5B were unchanged in the subsequent two STM images. However, in the third image taken after Figure 5B, the \( \text{PH}_2 \) molecule has diffused back to its original position, as shown in Figure 5C. In 20 STM images
acquired over a period of 1 h, the PH$_2$ molecule was imaged in its rightmost position 13 times and in the leftmost position 7 times. The PH$_2$ molecule may have moved many more times than is indicated by these 20 images, as we effectively only observed its position once every three minutes. However, we can say that the two hemihydride dimers present low-energy sites for the PH$_2$ molecule to reside in with a reasonably low energetic barrier for diffusion and that the molecule was not observed to reside in any other position on the surface during the hour that we imaged it.

In Figure 5D, we have a departure from the diffusing of the PH$_2$ molecule from one location to the other; we now see a PH + 2H protrusion at the top right position and a hemihydride in the lower left position. The PH + 2H protrusion is accompanied by a one-dimer-wide depression on its left side, known to be characteristic of its appearance in filled-state STM images. At some time between the images shown in Figure 5C and D, the PH$_2$ molecule has dissociated to PH as discussed in Section 5; i.e., the PH$_2$ molecule has shifted across to occupy a dimer-bridge position on the neighboring Si dimer and subsequently dissociated via a proton-shift reaction. The proton shift is back toward the adjacent hemihydride dimer, resulting in the formation of a monohydride dimer that appears dark in the STM image and produces the depression seen adjacent to the PH + 2H protrusion in Figure 5D.

The hemihydride dimer shown in Figure 5D remained unchanged for the next 70 min, during which it was imaged, in agreement with the energetic calculations presented in the previous section. The PH + 2H feature in Figure 5D further dissociated to a U-shaped P + 3H feature (not shown; we have described the spontaneous dissociation of PH to this U-shaped feature previously). 5 min after the image shown in Figure 5D was acquired and remained in this state for the remainder of the time it was imaged, more than an hour.

Figure 6 shows a pair of images of a lightly PH$_3$ dosed Si(001) surface, where we see a diffusion and dissociation event similar to that shown in Figure 5. In this case, however, we see the diffusion of the PH$_2$ molecule to extend much farther along the dimer row (~15 nm) before dissociation. In Figure 6A, we see a PH$_3$ + H feature indicated by an arrow in the lower right of the image and a hemihydride dimer indicated by an arrow at the top left of the image. Figure 6B shows an image of the same surface area taken 3 min later. We see in this image that the PH$_2$ molecule has diffused along the dimer row toward the top left of the image. Upon reaching the site of the hemihydride dimer, the PH$_3$ molecule dissociates to PH + 2H in a manner analogous to that seen in Figure 5. Figures 5 and 6 show two examples of the surface diffusion and dissociation of PH$_2$ on Si(001) that has been observed routinely in our experiments.

It is worth pointing out that the mechanism by which PH$_2$ diffuses along the dimer row is closely related to the mechanism for the dissociation of PH$_2$ to PH. As we discussed in Section 5, the first stage of PH$_2$ dissociation (from the asymmetric B1 structure) involves a shift of the PH$_2$ molecule from the end of one Si dimer to the end of the adjacent dimer. This shift is facilitated by the lone pair orbital of the PH$_2$ molecule (note the PH$_2$ has a lone pair because it has a third bond to a Si atom on the surface), forming a dative bond with the nucleophilic site of the adjacent Si dimer. Diffusion of the PH$_2$ molecule along the row occurs when this shift is repeated for successive dimers along the dimer row. As shown in Figure 6, we have observed the anisotropic diffusion of PH$_2$ to occur over distances up to 15 nm before dissociating to PH at the site of an existing defect such as a hemihydride dimer or existing PH molecule. This leads us to speculate that the probability of the PH$_2$ molecule shifting into the B4 configuration (Figure 4A) and subsequently dissociating to PH + 2H (C1) is greatly enhanced by the presence of such defects in the dimer row. Thus, we believe that the formation of short chains of PH + 2H features on saturation-dosed surfaces (such as seen in Figure 2B) can be attributed to the anisotropic diffusion of PH$_2$.

The fact that it is the lone pair orbital of the PH$_3$ adsorbate that facilitates its anisotropic diffusion explains why we do not observe diffusion for species such as the PH + 2H adsorbate. However, by analogy, we expect that this diffusion mechanism will be important for other molecules adsorbed to Si(001) that have lone pair orbitals, such as AsH$_3$.

The data presented here are in good agreement with previous studies using alternative surface science techniques. Colaianni et al. have shown that all PH$_3$ dissociates to PH$_2$ upon adsorption to Si(001) at room temperature and that all PH$_2$ is completely dissociated after annealing to ~375 °C, in excellent agreement with our results (we have reported the complete dissociation of PH$_3$ after annealing to ~350 °C in Ref 3). A subsequent key paper by Shan et al. used FTIR to conclude that the adsorption of PH$_3$ to Si(001) was only partially dissociative at room temperature and the majority species was molecularly adsorbed PH$_3$. However, as we have discussed in detail in a previous report, we believe the data in this paper can be reinterpreted in a sensible and straightforward way that makes it consistent with our results; essentially, the triplet group of infrared P−H stretch modes assigned to PH$_3$ by Shan et al. should instead be assigned to PH$_2$. Vibrational frequency calculations performed using the Gaussian package suggest that PH$_3$ will produce a single high-intensity peak with a doublet of smaller peaks, unlike the three peaks of similar intensity reported by Shan et al. The same calculations suggest that PH$_2$ will produce four stretch modes (two each from two different conformations), but two of the peaks are closely spaced and might therefore be observed as a single peak. A more recent paper by Lin et al. reports the appearance of two dominant adsorbate species in XPS data and assigns these to PH$_3$ and PH$_2$. However, no additional experimental evidence for assigning the adsorbates as PH$_3$ and PH$_2$ is presented by Lin et al., and when instead interpreted as PH$_3$ and PH, their data is in good agreement with the results we have presented here. Finally, our interpretation is in good agreement with all DFT calculations and STM measurements so far reported for this system in contrast to the interpretation of partially dissociative adsorption, which is at odds with these reports.
We make two general comments on the study of adsorbates with STM: (1) The data we have presented reinforces the point that, when analyzing STM images of adsorbates on semiconductor surfaces, it is not sufficient to consider only features that appear as protrusions above the surface plane. We have shown that \( \text{PH}_2 \) molecules are imaged on the Si(001) surface with an apparent intensity that is equal to the surrounding silicon dimers. This is undoubtedly the reason that this molecule remained unidentified until it was imaged within lithographic patches on H-terminated Si(001) surfaces such as in Figure 1. (2) We note the importance of observing transitions between successive STM images in identifying adsorbates. By observing such transitions and carefully comparing the results with ab initio calculations, we have been able to identify the diffusion of \( \text{PH}_2 \) molecules on Si(001) and their subsequent dissociation.

In summary, we have performed a combined STM/DFT study of the adsorption of \( \text{PH}_3 \) to Si(001) at room temperature and 120 K. At room temperature, we find the adsorption is dissociative, producing both \( \text{PH}_2 \) and \( \text{PH} \) adsorbate species. \( \text{PH}_2 \) adsorbates are predominantly found as part of a \( \text{PH}_2 + \text{H} \) structure where each fragment is bound to opposite ends of a single dimer, and this produces a feature that appears asymmetric about the dimer row in STM images. \( \text{PH} \) is generally found with the \( \text{PH} \) fragment bound in a dimer-bridge position about a single Si dimer and the two dissociated H atoms bound to an adjacent Si dimer. The appearance of this feature in filled-state STM images is a bright circular protrusion (PH) with an adjacent dimer-sized depression (\( \text{Si}-\text{Si}-\text{Si} \)). The relative coverage of these two adsorbate species is dependent on the \( \text{PH}_3 \) dose rate because the dissociation of \( \text{PH}_3 \) to \( \text{PH} \) occurs on a time scale of minutes. At 120 K, the dissociation of \( \text{PH}_2 \) to \( \text{PH} \) is completely inhibited but begins to occur upon warming to 200 K. By studying low-coverage surfaces at room temperature, we have observed the in situ diffusion and dissociation of \( \text{PH}_2 \). DFT calculations show that this diffusion is facilitated by the lone pair orbital of the \( \text{PH}_2 \) adsorbate, and we therefore expect this mechanism to be important for other molecules bound to Si(001) that have lone pair orbitals. \( \text{PH}_2 \) is responsible for the formation of hemihydride dimers on the low \( \text{PH}_3 \) dosed Si(001) surface and the lining up of \( \text{PH} \) molecules along dimer rows on Si(001) surfaces at saturation coverages. The data we present here has important implications for the fabrication of atomic-scale P dopant structures in Si. In addition, the principles of molecular identification using STM that we have presented here will be of interest to researchers in related fields such as molecular electronics.

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References and Notes