Atomic-scale observation and control of the reaction of phosphine with silicon

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The ability to identify and control the pathway by which chemical reactions occur at the level of individual atoms will be of enormous benefit in the coming age of nanotechnology. Here, we present a detailed atomic-resolution scanning tunneling microscopy (STM) study of one such pathway: the adsorption, surface diffusion and dissociation of phosphine (PH$_3$) on silicon (001). We show that PH$_3$ dissociates on Si(001) to produce PH$_2$ + H, PH + 2H and P + 3H moieties. In addition, we show that PH$_2$ molecules are readily able to diffuse on Si(001) at room temperature, resulting in the formation of hemihydride dimers on low dosed Si(001) surfaces. In addition we show that control over the processes of diffusion and surface incorporation can be achieved using STM-based hydrogen lithography; a technique that is now used in many STM laboratories. [DOI: 10.1380/ejssnt.2006.609]

Keywords: Scanning tunneling microscopy; Density functional calculations; Surface chemical reaction; Phosphine; Silicon

I. INTRODUCTION

The ability to controllably position dopant atoms in semiconductors with atomic-scale precision has great potential for the creation of atomic-scale electronic devices, for example silicon single-electron transistors, quantum cellular automata [1, 2], and when the control is extended to individual dopant atoms [3], devices such as a single-dopant transistor [4], or a silicon-based quantum computer [5–7]. The development of routine methods for positioning individual dopant atoms requires a precise knowledge of the physics and chemistry of each of the stages in the fabrication strategy. We have recently demonstrated using first-principles calculations and scanning tunneling microscopy (STM) observations [8, 9] that the interaction of phosphine (PH$_3$), a commonly used P precursor molecule, with the technologically important silicon (001) surface is much more complex than previously thought [10, and references therein]. In addition, while STM is an extremely good technique for observing surface adsorbate species, it is often very difficult to unambiguously identify the exact chemical nature (dissociation state, surface bonding geometry etc.) of the features observed in the images. Here we present the results of a detailed STM study of the interaction of PH$_3$ with the Si(001) surface. We identify adsorbed PH$_2$, PH and P monomer species. In addition we present the direct observation of PH$_2$ diffusion and dissociation on Si(001). Finally, we demonstrate how H-lithography [11, 12] can be used to limit the spatial extent of the reaction of PH$_3$ with Si(001) and when combined with a ∼350°C anneal can result in control over the positioning on individual P atoms into the Si(001) surface with nanometer accuracy.

II. EXPERIMENTAL

Experiments were performed using a commercial STM (Omicron Vacumphysik GmbH, variable temperature STM) inside an ultra-high vacuum (UHV) chamber with base pressure < 5 × 10$^{-11}$ mbar. Silicon wafers with $10^{15}$ cm$^{-3}$ P doping were used in all experiments. Care was taken to avoid sample contamination by using only ceramic tweezers to handle the samples and UHV sample holders constructed from tantalum, molybdenum and alumina ceramic. Sample preparation was performed in the standard way [13] 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. PH$_3$ gas was admitted to the STM chamber via a leak valve with line-of-sight to the sample while mounted in the STM and no hot filaments were close by or in line-of-sight to the sample during dosing.

III. RESULTS AND DISCUSSION

Figure 1 shows filled- and empty-state STM images of four of the most common surface adsorbate species that we have observed in our STM experiments after exposing Si(001) surfaces to submonolayer coverages of PH$_3$. The adsorption of PH$_3$ to Si(001) is dissociative, producing PH$_2$ + H bound to opposite ends of a single Si dimer, as shown in Fig. 1(a). Further dissociation of the PH$_2$ molecule can result in the formation of PH bound onto of a single Si dimer in a dimer-bridge site and a monohydride dimer, as shown in Fig. 1(b). We have observed this dissociation process to take place on a time scale of tens of min-

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Dissociated H atoms and has a state STM images. All STM images are giving this feature a U-shaped appearance. (b) PH bound onto a single Si dimer in a dimer-bridge site. (c) A P monomer is bound between the ends of two neighbouring Si dimers with the three dissociated H atoms producing the dark regions seen in the STM images, giving this feature a T-shaped appearance. (d) A P monomer is bound in an end-bridge configuration located away from its dissociated H atoms and has a T-shaped appearance in empty-state STM images. All STM images are ∼4 × 4 nm².

Figure 2: (a) Si(001) surface dosed with 0.0015 L PH₃. (b) An enlargement of the boxed area in (a) showing a single PH₂ + H feature. (c) This image, acquired two minutes after (b) shows a centered PH + 2H feature where the PH₂ + H feature was, indicating the the PH₂ molecule has dissociated in the time between when the two images were acquired. (d) and (e) Schematic diagrams corresponding to (b) and (c). Parameters for all images was −2 V and 0.2 nA.

utes, as will be discussed further below. The PH₂ and PH moieties shown in Figs. 1(a) and 1(b) are by far the most commonly observed adsorbates on PH₃-dosed Si(001) surfaces, however, we routinely observe three other adsorbate species. Two of these are shown in Figs. 1(c) and 1(d), consisting of a P monomer bound in end-bridge configuration, while the third is a hemihydride dimer that consists of a single H atom bound to one end of a Si(001) dimer (not shown in Fig. 1, see Figs. 4, 5).

Figure 2(a) shows a 35 × 35 nm² area of a Si(001) that has been exposed to 0.0015 L PH₃. This image was acquired approximately 30 minutes after PH₃ dosing. A close examination of this surface reveals a uniform coverage of PH₂-related adsorbates, predominantly the asymmetric PH₂ + H and centred PH + 2H adsorbates that we discussed in Figs. 1(a) and 1(b). Figure 2(b) shows an enlargement of the boxed area in Fig. 2(a) where a single PH₂ + H feature can be seen close to a step edge. The image shown in Fig. 2(c) is the same area of the surface shown in Fig. 2(b) but acquired two minutes later. In this image we see that there is now a centered PH + 2H feature where the PH₂ + H feature was, indicating the the PH₂ molecule has dissociated in the time between when the two images were acquired, as indicated by the schematic diagrams in Figs. 2(d) and 2(e). We have observed dissociation events like this to occur on a time scale of tens of minutes, resulting in the coverage of PH₂ (PH) decreasing (increasing) as the surface is imaged over a period of an hour. We have also observed the further dissociation of PH to form both of the P monomer species shown in Figs. 1(c) and 1(d). While we have observed the dissociation of PH to P on numerous occasions, the frequency of such events at room temperature is much less than the dissociation of PH₂ to PH. However the frequency of these events can be greatly increased by raising the substrate temperature slightly to ∼200°C, which greatly increases the density of P monomers directly bound to the surface. Figure 3 shows an image of a Si(001) surface that was exposed to a light dose of PH₃ while at a temperature of 200°C. In this image we see that the majority adsorbate species is the U-shaped P monomer species, while there are only 4 bright protrusions, which are either undissociated centred PH features, or perhaps ejected Si addimers resulting from the incorporation of some P into the surface. This is consistent with the dissociation from PH to P being an activated process with an increased probability for occurring at elevated temperature.

In addition to the direct dissociation of PH₂ to PH we have also observed the surface diffusion of PH₂ molecules, which is often accompanied by the PH₂ molecule dissociating to PH at a different location on the surface from the original PH₂ + H site. Two examples of this can be seen in Fig. 4. In Fig. 4(a) we see a PH₂ + H feature (left arrow) and a hemihydride dimer (right arrow), which are on adjacent dimer rows and separated by a distance of about 15 nm. The image shown in Fig. 4(b) is of the same area of the surface acquired three minutes later. In this image we see that the PH₂ molecule in Fig. 4(a) has diffused from left to right along the dimer row and dissociated at the site of the hemihydride dimer in Fig. 4(a) to form a PH + 2H feature at the right arrow while leaving a
hemihydride dimer at the site of the left arrow. Note that the diffusion of the PH$_2$ is anisotropic, occurring predominantly along the dimer row, but at the site of the hemihydride dimer the PH$_2$ jumps across to the adjacent row. We have observed this behaviour on numerous occasions in our experiments and thus conclude that the presence of a hemihydride dimer in the adjacent dimer row lowers the energy barrier for the PH$_2$ molecule to hop across the dimer row. Similarly, in Figs. 4(c) and 4(d) we see that a PH$_2$ molecule diffuses away from a PH$_2$ + H feature and dissociates to PH + H at the step edge, as indicated by the arrows on the images. While in both of the examples shown in Fig. 2 the PH$_2$ molecule dissociates to PH after diffusing, we have also observed the diffusion of a PH$_2$ molecule between two nearby hemihydride sites without dissociation. An example of this can be seen in Fig. 5, where a PH$_2$ molecule diffuses away from a PH + H feature to an adjacent hemihydride dimer site, with the net result that the two features switch places. We have observed the diffusing back and forth of a PH$_2$ molecule between adjacent hemihydride dimer sites for periods of more than an hour before eventually dissociating to PH (not shown).

The motivation for this study of the interaction of PH$_3$ with Si(001) is to develop the capability to position individual P atoms into Si(001) with atomic-scale precision. Our strategy for achieving this control [14] is shown in Fig. 6(a). First, a Si(001) surface is passivated by adsorbing a single monolayer of H atoms to it. The second step is to lithographically pattern this H layer by removing individual H atoms with the tip of a STM. The third step is to expose this lithographically patterned surface to PH$_3$ gas, allowing PH$_3$ molecules to adsorb to the reactive areas of bare Si(001) exposed by the STM tip. Finally, the fourth step is to thermally dissociate the adsorbed PH$_3$ molecules, resulting in the individual P atoms from these molecules taking up substitutional lattice sites in the top layer of the substrate to form P-Si heterodimers; this surface incorporation of P atoms was first reported by Hamers and coworkers [15] and has been revisited in recent publications [16].

Figures 6(b) — 6(e) demonstrate the successful completion of the fabrication strategy shown in Fig. 6(a). Figure 6(a) shows a H-terminated Si surface with a controlled desorption site of diameter ∼ 1 nm, exposing just two or
FIG. 6: (a) Process summary for positioning individual P atoms into Si(001). (b), (d) H-terminated Si(001) surface with one and three, ∼1 nm diameter H-desorption points, respectively. (c), (e), After exposure of the surface to 0.3 Langmuir PH$_3$ and annealing to 350°C for 10 seconds a single P atom has been incorporated into the surface in the form of a P-Si heterodimer in each of the lithographically defined areas.

three of the substrate Si dimers. Figure 6(b) shows the same surface area after dosing with ∼0.3 L PH$_3$ and annealing to ∼350°C. In this image we can see the characteristic signature of a H-terminated P-Si heterodimer (P-Si-H), which appears as an asymmetric protrusion about the dimer row. The arrows in Figs. 6(b) and 6(c) indicate that this P-Si heterodimer occurs within the original lithography region in Fig. 6(b), as can be confirmed by comparing to the location of the surface defect in both images (depression on left hand side of the images). Notice also that there is a complete H re-termination of the lithographic between Figs. 6(b) and 6(c), which is a result of the adsorption of the dissociated H atoms from the original PH$_3$ molecule.

Similarly, Figs. 6(d) and 6(e) show the incorporation of three individual P atoms within three H-lithography desorption point separated by ∼15 nm. The three lithography desorption points can be seen in Fig. 6(d). After PH$_3$ dosing and annealing a single P atom is incorporated within each of these lithographic sites, as seen in Fig. 6(e). Again, each incorporated P atom can be identified by its characteristic asymmetric appearance about the Si dimer row. In addition to the incorporated P atoms in Fig. 6(e) we see several bright white protrusions. These protrusions can be attributed to either dangling bonds created by H desorption events during the 350°C anneal, or the presence of surface Si atoms that have been ejected from the surface during P atom incorporation, and do not affect the P atom placement. The result shown in Figs. 6(d) and 6(e) is significant for the creation of the Kane P in Si quantum computer [5], which requires the positioning of P atoms in Si separated by ∼20 nm.

IV. CONCLUSION

We have performed a detailed STM-based investigation of the interaction of PH$_3$ with the Si(001) surface. By combining these STM observations with our previous quantum chemistry calculations [8, 9] we have been able to identify PH$_3$-related adsorbates on the surface. PH$_3$ was found to adsorb dissociatively to form predominantly PH$_2$ and PH species at room temperature. The initial distribution of PH$_2$ and PH was found to change over a period of about an hour, with the density of PH$_2$ molecules decreasing in favour of an increasing density of PH and to a lesser extent bound surface P monomers. We have shown STM images of the real-time dissociation of these molecules from PH$_2$ to PH. The dissociation of PH$_2$ to PH is sometimes preceded by the surface diffusion of PH$_2$. Finally, we have shown that H-lithography can be used to limit the spatial extent of the reaction of PH$_3$ with Si(001). By first controlling the location of the adsorbed PH$_3$ molecular fragment and subsequently annealing the substrate to 350°C we have been successful at incorporating individual P atoms into the Si(001) surface with a spatial accuracy of ∼1 nm.

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