Enhanced Atomic Precision Fabrication by Adsorption of Phosphine into Engineered Dangling Bonds on H-Si Using Scanning Tunneling Microscopy and Density Functional Theory

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Abstract

Doping of Si using the scanning probe hydrogen depassivation lithography technique has been shown to enable placing and positioning small numbers of P atoms with nanometer accuracy. Several groups have now used this capability to build devices that exhibit desired quantum behavior determined by their atomistic details. What remains elusive, however, is the ability to control the precise number of atoms placed at a chosen site with 100% yield, thereby limiting the complexity and degree of perfection achievable. As an important step towards precise control of dopant number, we explore the adsorption of the P precursor molecule, phosphine, into atomically perfect dangling bond patches consisting of 3 adjacent Si dimers along a dimer row. Using low temperature scanning tunneling microscopy, we identify the adsorption products by generating and comparing to a catalog of simulated images, explore atomic manipulation after adsorption, and follow up with incorporation of P into the substrate. Imaging after incorporation indicates that, for saturation dosed perfect lithographic patches, controllable placement of single atoms may have higher yield than previously expected. Based on the observations made in this study, we propose approaches that can be used to fabricate devices where it is ensured that each site of interest has exactly one P atom.

Keywords: STM image simulation, atomic precision, atomic manipulation, phosphorus doped silicon, hydrogen depassivation lithography
A quantum material or device is one whose functionality cannot be described by classical mechanics but rather fundamentally depends on the quantum properties that emerge from its precise geometrical and chemical makeup. In this regard, the ideal means to fabricate such a device would be to have absolute control over the placement of every constituent atom that makes a device, or at a minimum the key atoms which determine performance; for example, a transistor that operates based on the charge state of a single atom (Figure 1a) requires placement of exactly one P atom in a silicon matrix with nanometer precision positioning relative to nearby electrodes. While the necessary level of control is generally considered beyond the scope of standard fabrication techniques, it has been demonstrated for the class of electronic devices defined by precision doping of silicon. Both specialized ion implantation and scanning probe-based lithographic techniques have shown promise in the placement of phosphorus atoms at well-defined positions within a silicon crystal for use in quantum applications. In the case of ion implantation, a windowed mask can be used to achieve precision positioning control of the atoms while at the same time an electrical feedback mechanism can be used to monitor implantation events to ensure that precisely one atom gets imbedded; however, the limitation of this method is that there is some positional uncertainty both in the z direction (the direction normal to the surface) as well as laterally, resulting in a positional uncertainty of ~30 – 50 nm. In contrast, the scanning probe-based hydrogen depassivation lithography (HDL) technique which uses a scanning tunneling microscope (STM) tip to controllably remove hydrogen atoms from the H-Si (100) surface (see Figure 1b) is able to position P atoms to within a nanometer (here the remaining H atoms act as a mask to subsequent PH₃ deposition). While HDL is in fact able to achieve atomically perfect lithography, it does not guarantee perfect dopant incorporation at a lithographic site so that true deterministic control over the number of P atoms placed has not been demonstrated.
It is important to point out that HDL has been used to fabricate devices that have resulted in single P atom precision; for example, there have been two single atom transistors made to date\textsuperscript{2,3} where single P atoms have been placed with nanometer precision relative to source/drain leads and gate electrodes patterned in the same atomic plane and embedded in Si (see Figure 1a). A number of donor-dot qubit style devices where 1 or a few P atoms are placed in proximity to an island of P atoms (the dot), allowing for spin selective loading and unloading on the donor, have also been fabricated\textsuperscript{4–7}; for these devices, functionality is significantly impacted not only by precise control over tunnel coupling between the donor and the dot but also in requiring that the donor number be exactly 1 P atom (or some other controlled number of P atoms depending on the desired behavior), which is currently not possible as there is typically an uncertainty of one dopant atom per site. The reasons for uncertainty in the number of P atoms imbedded in these devices are twofold: the first is that in order to properly mask the surface the STM-based removal of hydrogen should be perfect to the last atom. This is a sufficiently challenging task that it was generally not attempted in the HDL devices mentioned above (as determined by inspection of post-lithography STM images from the respective studies). The second reason for potential failure in single atom placement is that even if the lithography is perfect, the chemistry that occurs when adsorbing and breaking down the precursor molecule (PH\textsubscript{3}) is naturally subject to some degree of randomness and may not always produce the desired outcome.

Based on results from several STM and Density Functional Theory (DFT) studies of PH\textsubscript{3} adsorption on Si surfaces\textsuperscript{8–12}, it has been inferred that if the STM is used to remove 6 H atoms from H-Si (100) as illustrated in Figure 1b, the likely outcome after depositing PH\textsubscript{3} and then heating to incorporate P into the Si lattice is that 1 P atom will be placed at the lithographic site. We refer to such lithographic patterns as 3-dimer patches because they are composed of 3 consecutive Si dimers along a dimer row, each dimer exposing 2 dangling bonds to which adsorbates can stick. Preliminary study of small lithographic structures\textsuperscript{13} suggests that there is a 30% chance that 0 P atoms could incorporate at the chosen site which
would fundamentally undermine the functionality of a device intended to be comprised of single P atom components. Based on this finding, the single atom transistor of ref\textsuperscript{3} was designed with a lithographic patch large enough to house more than one P atom; only after electrical transport measurements was it determined that the key transistor component in fact consisted of a single atom.

Within the field of research on HDL defined quantum devices this has thus far been the preferred way to deal with uncertainties in the number of atoms incorporated: specifically, to design and fabricate systems whose functionality is tolerant to such variation and construct lithographic structures larger than the ideal 3-dimer patch. However, it will ultimately be necessary to move beyond the level of control currently available to the HDL method and develop ways to achieve greater precision. A case where this has become particularly apparent is in the use of donor arrays for analog quantum simulation (AQS) where we have been able to make significant progress with devices that include some disorder\textsuperscript{14}. Such AQS systems can be qualitatively linked to an extended Hubbard model, but in order for them to be effective as a quantitative tool the chemical potential and on-site interactions at each array element will need to be precisely defined. This can only be done by fixing the number of P atoms exactly.

Achieving true single atom precision doping using HDL is a significant technological challenge requiring a more methodical approach to investigating PH\textsubscript{3} adsorption and P incorporation into nanoscale lithographic structures than what has been performed in previous experiments. In the present work, we focus on the question of what adsorption configurations occur when PH\textsubscript{3} is deposited into 3-dimer patches and how they correlate with incorporation outcomes. We use feedback-controlled lithography (FCL)\textsuperscript{15}, the methods of which are detailed in ref\textsuperscript{16}, to fabricate atomically perfect 3-dimer patterns as shown diagrammatically in Figure 1b and experimentally in Figure 1c; this distinguishes the present work from previous efforts as each adsorption site is guaranteed to be defect free and have atomically precise, controlled geometry. We then deposit PH\textsubscript{3} gas which selectively chemisorbs into the 3-dimer patches after undergoing a dissociation reaction in which at least one H atom is removed, typically attaching to a
nearby dangling bond (notably we find that this might not always be the case). In order to identify what the resultant adsorption structures are we image them with STM (see methods for details). The interpretation of the acquired images is not straightforward and requires an in-depth analysis if the identity and placement of molecules is to be properly determined. We address this by performing DFT calculations to simulate possible adsorption configurations for PHₓ in 3-dimer patches and generating simulated STM images which can be compared to experimentally acquired images. If we can find a match between a simulated image and an experimental one, then we can conclude the atomic input geometry used to generate the DFT image represents the correct configuration. The supercell and basic atomic setup used for image simulation is shown in Figure 1b. After identification, we then heat the sample to incorporate P into the substrate and image the resultant surface. Based on these post incorporation images we determine for each case whether it yielded successful P incorporation.

Figure 1. STM patterning for fabrication of single atom devices. (a) Schematic of an encapsulated single atom transistor device. (b) Atomic structure of the H-Si (100) surface where hydrogen (white atoms) has been removed from 3 consecutive Si (blue atoms) dimers on a single dimer row, illustrating the geometric setup used for DFT calculation of simulated STM images in this study. Image simulation is performed on a 10 layer slab, with a reconstructed hydrogen terminated surface on top, and hydrogen termination on the bottom (bottom-left inset) that mimics coordination to bulk silicon atoms. The bottom-right inset shows a possible saturation dose adsorption configuration of 3 PHₓ molecules. (c) STM empty (top) and filled (bottom) states images acquired on a single 3-dimer lithographic patch; indicated voltages are the sample bias and the inset scalebar shows the separation between two dimer rows of 0.77 nm.
Results and Discussion

In order to determine what adsorption configurations are possible, we first consider the likely molecular species that will result from attachment of the PH$_3$ precursor to the surface as well as to what sites a given molecule can bond. While PH$_3$ can bond to the surface directly, it dissociates quickly$^{8-10}$ into the products PH$_2$, PH, and P. We first use DFT calculations with the reduced supercell shown in Figure 2a to determine the energetic minimum geometries. To save computation time, we allow only the 6 Si atoms of the 3-dimer patch to relax in addition to the constituent atoms of the adsorbed molecule. By trying multiple possible adsites for each species (top, bridge, and hollow) and then allowing the system geometries to relax according to DFT calculated forces, we find that the preferred adsites are as shown in Figure 2b-f; these results are in good agreement with previous calculations$^{8,9}$. We also confirm that Si dimers prefer to buckle as shown in the side view of Figure 2g, and that they do so in an alternating manner along the dimer row consistent with the standard c(4x2) reconstruction of the Si (100) surface$^{17}$. Once a Si atom is coordinated to at least one additional atom, however, its associated dimer flattens as shown in the side view of Figure 2h.
Figure 2. DFT relaxation of atomic coordinates on a reduced supercell. (a) Reduced setup details: the slab consists of 3 Si layers, with all atoms fixed in position except for the 6 Si atoms for which hydrogen termination has been removed (outlined in green), as well as any adsorbates placed into the 3-dimer patch. (b–f) Final energetic minimum geometries for adsorbed PH$_x$ species demonstrating that (b) PH$_2$ prefers top-sites, (c,d) PH prefers bridge sites, and (e,f) P also prefers bridge sites. (g) Side view of a relaxed dimer showing that the energetically preferred configuration is in a buckled state. (h) Side view of a relaxed dimer with 1 hydrogen atom adsorbed demonstrating that the dimer becomes un-buckled once at least 1 Si atom has coordinated to an additional species.

Based on this information, we generate a comprehensive list of all possible adsorption configurations that might occur upon dosing PH$_3$, with the following additional assumptions: 1) a surface Si atom can be coordinated to at most 1 additional species (the Si atoms are already bonded to 3 other Si atoms), 2) Si-Si bonds, including the dimer bonds, will not break in order to accommodate bonding to PH$_x$, and 3) while we do allow adsorbed H atoms to leave the 3-dimer patch during adsorption, we do not allow addition of any new H atoms that weren’t already adsorbed or otherwise part of the precursor PH$_3$ molecule (e.g. if a single PH$_3$ molecule bonds to the patch, there can be at most 3 H atoms that stick to top sites, leaving behind a P atom bonded to a bridge site). This set of rules results in 622 total adsorption configurations (see section S1 of the supporting information for more details), which are then each geometrically relaxed using the DFT setup of Figure 2a. Once we have the set of relaxed coordinates for a configuration, we transfer the coordinates for the 6 Si atoms of the lithographic patch as well as those of the adsorbed molecules onto the larger slab of Figure 1b. For the larger system, we require all atomic positions to remain fixed, calculate the electronic ground state, and then use the integrated local density of states from the Kohn-Sham orbitals to simulate STM images for both filled and empty states. The result
is a catalog of simulated STM images that can be compared to experiment as a means to identify observed adsorption configurations; the full catalog is presented in section S6 of the supporting information.

Figure 3. Experimental and simulated STM images for saturation (a-f) and low dose (g-i) adsorption of PH₃ into 3-dimer patches. Image type is organized by column: experimental and simulated positive sample bias STM image, experimental and simulated negative sample bias STM image, ball-and-stick model of the identified adsorption configuration, and frequency of appearance, respectively. The frequency of appearance is expressed as a ratio of the number of times a configuration was seen divided by the number of 3-dimer patches that were patterned during the run (either the saturation dose, or the low dose run). All STM images in the STM+ column have a z (tip height) scale according to the color bar displayed at the bottom of the STM+ column, while those of the STM- are scaled according to their corresponding STM- color bar.
Figure 3 shows comparisons of the experimentally observed STM images with the DFT simulated images that have been identified as being the most likely matches. Also indicated are the number of observed instances of a given configuration during the experiment. Two experimental runs were performed, the first of which involved a low dose of PH$_3$ into a total of five 3-dimer patches (Figure 3g-i). During the second run, a set of nine 3-dimer patches was fabricated and the sample was subjected to a sufficiently high dose to achieve saturation (Figure 3a-f). One patch had no adsorption for the low dose, while all patches showed adsorption for the saturation dose.

With the ability to identify the adsorption configurations we now have insight into the chemistry of how PH$_3$ reacts with the optimal lithographic structure for single P atom incorporation (3-dimer patches, as predicted by previous DFT and un-passivated surface adsorption studies$^{8-11}$). The expected adsorption behavior was that dissociation products should form as a result of 1 H atom from a PH$_3$ molecule attaching to an empty site in a 3-dimer patch while PH$_2$ attaches to another empty site. Since there are 6 top sites, with a saturation dose there should be 3 PH$_2$ molecules and 3 H atoms in each patch; the proposed configuration$^{8,11}$ being that shown in the inset of Figure 1b, where the PH$_2$ molecules bond to separate dimers and alternate which side of the row they are on. What we find, however, is that the preferred configuration is that of Figure 3f with 2 PH$_2$ molecules on one side of the dimer row and the 3rd on the other; in fact, this configuration appears to be preferred over the previously predicted one as the alternating structure from the inset of Figure 1b was not observed.

A possible explanation for this behavior may be that there is some preference for PH$_2$ molecules to occupy the same side of a dimer row as one another as observed in Figure 3e. In addition, it appears that when a single PH$_2$ molecule bonds to the surface, the preferred adsite for the other hydrogen is on the adjacent dimer and on the same side of the row as evidenced by Figure 3h. Figure 3g,i are also consistent with this suggested preference. Notably these two adsorption behaviors are at odds with one another and create a competition as to which side of the dimer row a PH$_2$ will choose. In this case the
likely order of events would be that during the saturation dosing, the first PH₂ adsorbs as shown in configuration h, the second results in configuration g; the final PH₂ is forced to bond to the surface with its H atom across from it and so defaults to the preference of being on the same side of the row as its neighbor.

We also observe that in several cases the number of H atoms is not conserved (Figure 3b-d). For example, in Figure 3b there should be a total of 4 H atoms at top sites (2 from the PH, and 1 from each of the PH₂ molecules); in a 3-dimer patch, there are not enough top sites available for this to occur yet we still observe such configurations, implying that by some mechanism the remaining 2 H atoms must have left the vicinity of the 3-dimer patch. Given that this behavior is not seen in the low dose sample, we conclude that the additional H atoms are being driven off or reacting with other PH₃ molecules trying to bond to the patch, though the precise mechanism by which this happens is unclear.

For the saturation dosed sample, we performed two additional tests in order to investigate the link between adsorption structures and the desired outcome of single P atom incorporation into the Si lattice. The first test was to attempt modification of the adsorbed species using the STM tip; given the higher frequency of the configuration shown in Figure 3f, we chose one of these to perform feedback-controlled manipulation (FCM, using the same algorithm and procedure as FCL) with the tip positioned over the bottom-right PH₂ molecule as highlighted by the red arrow overlaid on the respective ball-and-stick model; we distinguish the procedure as manipulation, rather than lithography, because in this case we manipulate the adsorbed species instead of creating dangling bond patches for subsequent precursor molecule adsorption. The second test was to heat the sample to 275 °C for 2 minutes in order to perform incorporation (i.e. at least 1 P atom substitutionally replaces an underlying Si atom which is ejected to the surface). The results are shown in Figure 4.
Figure 4. STM images of incorporation and manipulation results imaged as ejected Si atoms. (a) Silicon atom imaged at a bridge site centered on the dimer row. (b) A silicon atom imaged at a bridge site on the edge of the dimer row. (c) An adsorption configuration of type (Figure 3f) after a manipulation attempt (pre-incorporation) using FCL. (d) Two ejected Si atoms imaged after incorporation at the site shown in (c). (e) Schematic of ejected Si at the center of the dimer row as imaged in (a). (f) Schematic of ejected Si on the edge of the dimer row as imaged in (b). The P incorporation positions of (a) and (b) are not known, so likely positions are illustrated in (e) and (f) as an aid to understanding.

We find that standard single atom incorporation STM images appear as those shown in Figure 4a,b where the ejected silicon appears either at a bridge site centered on a dimer row, or at a bridge site on the edge of the row. For the adsorption site where FCM was performed, the post-FCM image (Figure 4c) shows structure on two neighboring dimer rows and so cannot be compared to the catalog of simulated images to determine the precise resultant structure (the catalog contains images for single dimer row structures derived from 3-dimer patches); after incorporation, however, the resultant structure is that of two ejected Si atoms located at bridge sites on the edge of the dimer row (Figure 4d). We found ejected silicon atoms at all but one of the saturation dosed sites. The site with no ejected Si was expected because the STM tip unintentionally picked up all of the PH$_2$ at that location during imaging at negative sample bias; the adsorption configuration was that of Figure 4f for which we saw 4 copies, 2 of which were not manipulated and were found to result in a single ejected Si atom after incorporation. It should also be noted that for the configuration of Figure 3e, negative bias imaging caused an unintended modification
to the adsorption structure, but did not result in removal of all of the P atoms so that upon incorporation there was still an ejected Si.

In addition to the incorporation results, a number of other important observations can be made with respect to the data of Figures 3 and 4, which we discuss here. Identification of adsorbed PHx structures in STM images can be quite difficult, particularly since there are so many possible configurations. While it is not perfect (see section S2 of the supporting information for an example), comparison to the catalog of simulated images significantly narrows down the set of possible matches. Inconsistencies between the simulated STM image and the experimental image can arise for a number of reasons, the primary ones being: uncertainty as to the actual tip height above the sample (an arbitrary estimate must be chosen for image simulation), uncertainty in the mapping from DFT Kohn-Sham energies to sample bias, and tip-induced charging effects. The fact that not all atoms were relaxed (to keep computation time practical) and, that they were only allowed to relax on the reduced supercell of Figure 2a, may also play an important role in differences between simulated and calculated STM images in some cases. Additionally, details of the tip can affect details of the resultant image based on what tip orbitals are overlapping with sample states (e.g. s, p, d, or some mixture of them).

For the low dose configurations shown in Figure 3 where each has a Si dimer that does not participate in bonding, buckling behavior has an effect on the resultant STM image because imaging with an STM tip can potentially induce the buckled state to change\(^{16,18}\); in other cases the up/down atom (up and down in the context of buckling are illustrated in Figure 2g) can alternate more rapidly than the data acquisition rate, resulting in an image that is a thermal average of the 2 configurations, and in other cases the presence of a nearby defect can pin the dimer atoms in a fixed buckled state. For each configuration of Figure 3g-i we find that at positive sample bias the resultant image is best represented by averaging the 2 up/down buckled configurations. Averaging also gives the best results for the negative bias images of Figure 3g,i, but not for Figure 3h. For the latter, it appears that the dimer is pinned in the configuration
shown: the *up* atom is closest to the PH$_2$ (see supporting information section S3 for a comparison that illustrates this).

In the absence of simulated images, an alternative method of identification would be measurement of the topographic heights of various lobes in an STM image. It is immediately apparent that negative bias (filled states) images are preferable as can be seen in Figure 3a: in this case both PH$_2$ and PH appear to be the same height at positive bias, but are clearly different at negative bias. Figure S4 of the supplemental, however, shows that negative bias topographic heights do not consistently map to specific adsorbed species, particularly if there are neighboring dangling bonds. Analysis of the position of a molecule relative to the center of the dimer row may also aid in identification since PH$_2$ will never appear at a central bridge site, though this will not help in distinguishing PH from P.

For all of the sites where no manipulation (intentional in one case, unintentional in two others) was performed, there was 1 ejected Si implying incorporation of exactly 1 P atom. This is a key result as it suggests that for perfectly engineered 3-dimer patches that are saturation dosed with PH$_3$, incorporation yield may be as high as 100%. Given the relatively small population size of this study, a sample size of 6 (where manipulated cases have been excluded), it is reasonable to consider that the yield could however be lower (for a p-value of 0.05, the yield could be as low as 61%). Based on our results, therefore, we propose two feasible approaches that can be implemented to achieve true single atom incorporation using HDL and consider their relative strengths and weaknesses. The first is a 3-dimer patch approach: use FCL to fabricate perfect 3-dimer patches at desired single atom sites, saturation dose, incorporate, then re-terminate the surface with hydrogen, and finally use the STM to image the results. If any of the intended sites are missing an ejected Si atom, then it is likely that P did not incorporate and the STM can be used to re-fabricate a 3-dimer patch at the desired location and the procedure can be repeated. The second method we propose is a 1-dimer patch approach: fabricate 1-dimer patches, dose, then image those sites and perform FCM to remove H atoms from PH$_2$ (improving the chances of
incorporation), and proceed with incorporation and post incorporation imaging as described in the 3-dimer patch approach.

The 1-dimer approach has the advantage that the initial lithography step is significantly simpler (H atoms are removed from a single dimer rather than 3 neighboring dimers), but comes at the cost of added complexity and risk during the post-dose imaging, a step which may not be necessary for the 3-dimer approach. As observed in the present study, imaging after dosing carries with it some risk of unintentional tip manipulations (including complete removal of the adsorbed species); for the tip used in the saturation dose sample we found that negative bias imaging was particularly unstable. A second strength of the 1-dimer approach is that it ensures there can be no more than 1 P atom incorporated at a site; based on the incorporation results from this study there is reason to believe this is also not an issue for 3-dimer patches, however based on DFT calculations\textsuperscript{11,12} both PH and P may have low enough energy barriers to incorporation that in some cases (e.g. Figure 3a-d) two incorporations could be possible. While the proposed 1-dimer method is plausible (tip-induced H dissociation has been shown for PH\textsubscript{2} on clean Si (100)\textsuperscript{19}, and we saw increased yield with tip manipulation on a 3-dimer structure in Figure 4d), it remains to be proven experimentally. By comparison, the results of this study lend direct evidence for the efficacy of the 3-dimer method, particularly when one checks for ejected Si upon incorporation and repeats the procedure as necessary.

**Conclusion**

Summarizing the key results, we have studied adsorption of PH\textsubscript{3} into 3-dimer patches and followed up with subsequent P incorporation for saturation dosed structures. We find that the most common adsorption configuration is that of Figure 3f, that annealing resulted in incorporation for all saturation dosed configurations, and that STM tip-based manipulation using FCM enabled incorporation
of 2 P atoms at one site. Based on these results, we proposed two protocols for the fabrication of 100% yield single P atom-per-site structures using the HDL technique. The catalog of simulated STM images (see supplemental section S6) that was used in this study was instrumental in determining adsorption configurations, enabling a more in-depth look at the adsorption chemistry of PHx in designer lithographic patches as well as bringing to light behavior not previously predicted. Additionally, the ability to determine the species at each site will allow STM operators to make educated decisions as to how to respond to adsorption configurations seen while fabricating using HDL. As HDL techniques develop toward greater device complexity, it will become increasingly important to also control the number of P atoms at each site to be greater than one (e.g. ensuring exactly 2 P atoms incorporate); knowing where to place the tip and what manipulations to perform will require the precision identification enabled by the simulated image catalog. Some examples of devices that would benefit are singlet-triplet qubits\(^\text{20}\) consisting of a single P atom at one site within tunneling range of a second site with 2 P atoms, and AQS arrays\(^\text{14}\) where selected sites have a predetermined number of P atoms intended to induce a different chemical potential than sites with precisely 1 P atom. In this study we have presented a pathway to use HDL fabrication in development of devices and materials where the details of the Hamiltonian are engineered with absolute precision based on the number and placement of atoms in quantum structures.

**Methods**

**Sample and Tip Preparation.** H-Si (100) surfaces (the low dose and saturation dose studies were on separate samples) were prepared from 2.5 mm × 10 mm × 0.25 mm chips that were lightly p type boron doped at a density of \(10^{15}\) to \(10^{16}\) cm\(^{-3}\). The samples underwent standard chemical cleaning consisting of Base Piranha, RCA-1, and RCA-2, followed by introduction to ultrahigh-vacuum (UHV) at a base pressure of \(6 \times 10^{-11}\) mbar (\(6 \times 10^{-9}\) Pa). Samples were degassed at 600 °C for 12 hours via direct current heating,
then flashed to 1200 °C for 45 s; flashing was aborted to 600 °C whenever pressures went above $1 \times 10^{-8}$ mbar ($1 \times 10^{-6}$ Pa) and then resumed once pressures went below $2 \times 10^{-10}$ mbar ($2 \times 10^{-8}$ Pa). Hydrogen passivation was performed at 275 °C with H$_2$ gas backfilled into the vacuum chamber at a pressure of $2.8 \times 10^{-6}$ mbar ($2.8 \times 10^{-4}$ Pa) for 20 minutes; at the same time a W filament (7 W, 0.7 A) in line of sight to the sample was used to crack the H$_2$ molecules into their constituent atoms. The sample was then transferred to the STM UHV chamber with a base pressure below $4 \times 10^{-11}$ mbar ($4 \times 10^{-9}$ Pa).

The tip was prepared by electrochemically etching a polycrystalline W wire in KOH solution. It was then cleaned in vacuum by annealing for several hours before use. Final tip preparation was done by in situ modifications such as voltage pulses (up to 10 V) and current setpoint pulses (up to 300 nA).

**STM Setup.** All lithography and scans were performed using a Scienta Omicron LT STM at a temperature of 77 K. (Certain commercial equipment, instruments, or materials are identified in this paper to foster understanding. Such identification does not imply recommendation or endorsement by the national institute of standards and technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.) All biases quoted in the main text are specified as sample bias by convention, though in our setup the physically applied bias is to the tip while the sample is grounded. All images were acquired in constant current mode with the current setpoint specified at 50 pA. All positive bias images (empty states) were acquired at 2 V sample bias, and all negative bias images (filled states) were acquired at -2 V.

**PH$_3$ Dosing Details.** Phosphine was dosed directly into the STM chamber via a leak valve. The line preceding the leak valve (the dosing line) was filled with PH$_3$ gas to a pressure of $4 \times 10^{-3}$ mbar ($4 \times 10^{-1}$ Pa). The leak valve was then opened to backfill the STM chamber to a maximum of $4 \times 10^{-8}$ mbar ($4 \times 10^{-6}$ Pa). At cryogenic temperatures, it is not possible to maintain this pressure without refilling the dosing line, whereas if the STM chamber is at room temperature a refill is not necessary, implying that
maintaining a fixed pressure for a set amount of time is not an accurate method for determining dose at low temperature in our setup. As a means to estimate the dose, rather than refill the line we instead tracked the pressure drop. We applied a pressure drop of $1 \times 10^{-3}$ mbar in the dosing line which corresponds to a dose of 5.4 Langmuir ($4 \times 10^{-6}$ Pa for 3 minutes when the chamber is at room temperature). To achieve a saturation dose, we placed the sample on a wobble-stick in line of site to the leak valve. For the low dose, we left the sample in the STM, reducing exposure sufficiently that the same dosing line pressure drop resulted in a low dose; notably therefore, the saturation dose occurred on a room temperature sample (on the wobble stick) while the low dose was performed on a sample at 77 K. After dosing, the saturation dosed sample required relocation of the adsorption sites relative to fiducial marks; this was done by using large area scans to first relocate STM fabricated relocation features that were 400 nm $\times$ 1000 nm and had a known position relative to the 3-dimer patch sites (see section S5 of the supporting information for more details).

**DFT Calculations.** As detailed in the main text, Figures 1b and 2a show the atomic setups used for simulated STM images and adsorption geometries, respectively. We used the Perdew-Burke-Ernzerhof generalized gradient approximation\textsuperscript{21,22} for the exchange-correlation functional and a projector augmented wave basis with energy cutoff of 800 eV as implemented in GPAW\textsuperscript{23–25}. Initial atomic coordinates for Si and H atoms in the slabs of both setups were taken from previously relaxed slabs of optimum size for the relaxation problem as described in detail in reference\textsuperscript{16}. For subsequent atomic coordinate relaxation of adsorbates on the slab of Figure 2a, a force cutoff of 0.05 eV/Å was used. Both setups used a k-point mesh consisting of the $\Gamma$ point only. Simulated STM images were generated by integrating the local density of states (LDOS) as calculated by DFT, following the Tersoff-Hamann approach for an s-wave tip\textsuperscript{26}. It is also possible to consider alternative tip wavefunctions (i.e. linear combinations of s,p,d,f orbitals), however this was unnecessary as the s-wave simulated images already enabled identification of the adsorption configurations of this study from the simulated images. We assumed a tip
height of 0.4 nm above the H-terminated surface at the lower-left corner of an STM scan and extracted the integrated LDOS at that position. Images were then determined as surfaces of constant integrated LDOS using this value. Upon generating an image we additionally applied a Gaussian blur of \( \sigma = 0.77 \text{ nm} \) (cutoff radius = 1.54 nm) to mimic the blurring seen in the experimental images. It has been previously noted\(^{27} \) that Kohn-Sham eigen-energies can differ (often linearly with a scale factor and offset) from those inferred from experimental bias voltages; we found good agreement using integration limits of 0 to 1.1 eV for positive bias, and \(-0.9\) to 0 eV for negative bias.

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Supporting Information:

Enhanced Atomic Precision Fabrication by Adsorption of Phosphine into Engineered Dangling Bonds on H-Si Using Scanning Tunneling Microscopy and Density Functional Theory

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S1. Generating configurations.

We determine the set of all possible 3-dimer patch adsorption configurations by first considering the 3 possible species, the number of Si atoms they effectively occupy (e.g. bridge sites occupy 2 Si), and the maximum number of H atoms that as a result can occupy the remaining Si atoms in the 3-dimer patch. The maximum number of H atoms is determined by how many must have dissociated from a PH3 molecule in order to create the adsorbed species. Table S1 shows the possibilities considered.

| Species | Si atoms occupied | Max. H adsorption |
|---------|-------------------|-------------------|
| PH2     | 1                 | 1                 |
| PH      | 2                 | 2                 |
| P       | 2                 | 3                 |

Table S1. Site occupation and H dissociation characteristics for each PH3 derivative on the Si (100) surface. The “Si atoms occupied” column specifies how many Si atoms participate in bonding to the molecule, while the “Max. H adsorption” column specifies how many additional H atoms may appear on the surface as a result of dissociating from the original PH3 molecule.

To further determine the set of possible configurations, we construct the set of all physically possible combinations of numbers of PH2, PH, P, and H adsorbed into a patch together. The key
requirement is that the total number of Si atoms occupied is not allowed to exceed 6, or equivalently the number of sites available for H adsorption after the number of PH$_2$, PH, and P have been allotted must not be less than 0. This delineation of possibilities is shown in Table S2.

**Table S2.** Adsorption of multiple molecules into a 3-dimer patch. The first 3 columns are the number of each species adsorbed into the 3-dimer patch. “Top sites avail.” is the number of Si atoms still available to be bonded to after adsorption of the phosphine derivative species. “Max. H adsorbed” is the number of H atoms that must be removed from phosphine upon adsorption (first number) and the number that can remain in the 3-dimer patch based on site availability (second number). The final column are the numbers of H atoms in the 3-dimer patch used to generate configurations.

| PH$_2$ | PH  | P   | Top sites avail. | Max. H adsorbed | H     |
|--------|-----|-----|------------------|-----------------|-------|
| 6      | 0   | 0   | 0                | 6 → 0           | 0     |
| 5      | 0   | 0   | 1                | 5 → 1           | 1,0   |
| 4      | 1   | 0   | 0                | 6 → 0           | 0     |
| 4      | 0   | 1   | 0                | 7 → 0           | 0     |
| 4      | 0   | 0   | 2                | 4 → 2           | 2,1,0 |
| 3      | 1   | 0   | 1                | 5 → 1           | 1,0   |
| 3      | 0   | 1   | 1                | 6 → 1           | 1,0   |
| 3      | 0   | 0   | 3                | 3              | 3,2,1 |
| 2      | 2   | 0   | 0                | 6 → 0           | 0     |
| 2      | 1   | 1   | 0                | 7 → 0           | 0     |
| 2      | 1   | 0   | 2                | 4 → 2           | 2,1,0 |
| 2      | 0   | 2   | 0                | 8 → 0           | 0     |
| 2      | 0   | 1   | 2                | 5 → 0           | 0     |
| 2      | 0   | 0   | 4                | 2              | 2,1,0 |
| 1      | 2   | 0   | 1                | 5 → 1           | 1,0   |
| 1      | 1   | 1   | 1                | 6 → 1           | 1,0   |
| 1      | 1   | 0   | 3                | 3              | 3,2,1,0 |
| 1      | 0   | 2   | 1                | 7 → 1           | 1,0   |
| 1      | 0   | 1   | 4                | 4 → 3           | 3,2,1,0 |
| 1      | 0   | 0   | 5                | 1              | 1,0   |
| 0      | 3   | 0   | 0                | 6 → 0           | 0     |
| 0      | 2   | 1   | 0                | 7 → 0           | 0     |
| 0      | 2   | 0   | 2                | 4 → 2           | 2,1,0 |
| 0      | 1   | 2   | 0                | 8 → 0           | 0     |
| 0      | 1   | 1   | 2                | 5 → 2           | 2,1,0 |
| 0      | 1   | 0   | 4                | 2              | 2,1,0 |
| 0      | 0   | 3   | 0                | 9 → 0           | 0     |
| 0      | 0   | 2   | 2                | 5 → 2           | 2,1,0 |
| 0      | 0   | 1   | 4                | 3              | 3,2,1,0 |
Using the numbers of PH$_2$, PH, P, and H specified in Table S2, we construct all possible configurations. As a simple example, in the case of (PH$_2$, PH, P, H) = (1,0,0,0), there is only one molecule to be placed in the 3-dimer patch, a single PH$_2$. We generate a list of possible configurations where the PH$_2$ is placed at each of the 6 top sites. The remaining 5 top sites in each case are labeled with “up” or “down” to indicate dimer buckling, except for the Si atom across from the PH$_2$ which is labeled with an empty string, “”, to indicate that dimer has flattened (see Figure 2h of the main text). We also check the resultant list of configurations against itself and remove any configurations that are equivalent upon reflection across either the dimer row center axis, the perpendicular axis that runs through the two central Si atoms of the patch, or a combination of these two; notably the presence of up/down designations becomes important for low dose configurations where two cases that would otherwise be equivalent can be different from one another because of the buckled state of an empty dimer. When placing more than one species into the 3-dimer patch, we additionally apply the occupation rules illustrated in Figure S1. These rules ensure that each Si atom can participate in only 1 additional bond beyond its default surface configuration. The full catalog is shown in section S6.

**Figure S1.** Disallowed neighboring sites for subsequent adsorbates. Given an adsorbate placed at (a) a top site, (b) a bridge site on the center axis of the dimer row, or (c) a bridge site on the side of a dimer row, the large red X’s represent disallowed bridge sites while the small red x’s represent disallowed top sites.
S2. Catalog use in practice.

Figure S2. Identifying adsorption configurations using the catalog. Candidate configurations are those for which the positive bias simulated image appears to match experiment. Further narrowing down of possible matches can be done by comparing the negative bias images of the candidates.

There are many simulated images in the full catalog (see section S6) that appear similar to one another, complicating the process of making a precise identification. In cases like the example shown in Figure S2a, there may be multiple matches at positive bias but only one negative bias case agrees with the geometry seen experimentally: here, the first candidate configuration appears to be the most reasonable choice. This identification is complicated by the fact that the tunnel junction was unstable while imaging phosphine derivatives at negative bias, resulting in significant smearing along the fast scan direction. Despite this difficulty, none of the other candidate configurations of S2a present geometries that could reasonably be linked to what was seen experimentally.

For the case of Figure S2b, identification is not so straightforward as both positive and negative bias show multiple matches. We attribute the first candidate configuration as being the correct one, though this identification is not certain. Notably, even with the reduced certainty of S2b, the set of possible candidates has been reduced down to 5 (the key uncertainty is whether the 3rd species is PH or P). Given the increased brightness of the right-most lobe at positive bias in S2b which is not seen in the
experimental image (in fact, the leftmost lobe appears brightest in STM), we can likely also rule out the 4th configuration.

S3. Pinning vs. averaging of buckled dimers.

Figure S3. Comparison of simulated STM images for pinned and thermally averaged dimer buckling to the experimental STM image. Configurations used to generate each simulated image are shown above with “up” and “down” labels that denote the dimer buckling state corresponding to the same designations in Figure 2g of the main text. All images are at positive bias.

In the main text it was noted that the configuration of Figure 3f likely exhibits a pinned dimer (whereas the other low dose configurations do not). This determination was made by comparing the “pinned DFT” image to the “averaged DFT” image in Figure S3. We note that the upper lobe of the pinned image is more elongated in the vertical direction, matching more closely with what has been seen experimentally (the center image).
S4. Using negative bias height to determine species.

Figure S4. Comparison of apparent heights from selected configurations: (a) PH and PH$_2$, (b) 3 PH$_2$, (c) 2 PH$_2$ and 1 PH, and (d) 1 PH$_2$ and 4 dangling bonds. Labels are placed close to their respective species in the angled topographic view of the STM images, specifying the molecule type and its apparent height. For images with multiple PH$_2$’s of the same height, only one height is specified. Insets below each image show the corresponding adsorption configuration.

As a general rule of thumb, the apparent height of PH$_2$ should be less than that of PH which should be less than that of P. These expected height variations are based on the observation that H atoms on the molecules tend to cause a reduction of apparent height when imaged by STM (e.g. a dangling bond looks taller/brighter than a H terminated Si atom). When attempting identifications where a molecule is fully surrounded by H atoms (i.e. there are no neighboring molecules or dangling bonds), the apparent height should be sufficient to distinguish the adsorbed species. However, as shown in Figure S4, once there are neighboring species (including dangling bonds), there is overlap in the range of apparent heights measured for the different species. In the set of images shown, PH$_2$ ranges from 46 pm in height to 107 pm; this overlaps with the range seen for PH which varies from 104 pm to 107 pm, making it impossible to distinguish the two species by height alone.
S5. Relocating dimer patches.

![Figure S5](image.png)

**Figure S5.** Relocating 3-dimer patches. (a) Micron scale overlay of large range STM scans (grayscale) on fiducials (the file used to write the fiducials is displayed as purple marks). One example coarse walk path taken is shown in blue. (b) Zoom-in showing large scale pads written using HDL to aid in relocating the 3-dimer patches. (c) Ends of large scale pads pointing towards the sites where 3-dimer patches (orange) were written.

In our STM setup, procedures such as dosing and annealing (for incorporation) require removal of the sample from the STM stage. This means that after each of these steps, once the sample is remounted, the STM tip will no longer be positioned as it was previously: the location of the 3-dimer patches is generally shifted by 10s to 100s of microns relative to the STM tip. Our Si chips have etched fiducial marks which can be seen optically while approaching the tip and are also safe for scanning as can be seen in Figure S5a.

As a first step before fabricating any 3-dimer patches, we land on a fiducial mark and determine the scan region’s location relative to the fiducial. We coarse walk the scanner away from the fiducial while recording the number of steps traveled. Because we have calibrated our coarse motion, the recorded number of steps is a good estimate for the distance away from the fiducial that the 3-dimer patches will be fabricated. We then write and image a series of 3-dimer patches, followed by the use of HDL to write large pad features approximately 400 nm × 1000 nm (Figure S5b). These large scale features point towards the location of the 3-dimer patches as shown in Figure S5c.
When relocating the 3-dimer patches after dosing or annealing, we land on a known fiducial, then coarse walk to the recorded location of the 3-dimer patches. Using large area scans, we can see the pads that were written previously. To aid in this process we typically acquire both a constant current topography image as well as a dI/dV map. In some cases (particularly after incorporation), it may be difficult to see the pad in topography while dI/dV still shows good contrast. Once a large scale pad has been relocated, we switch to small image sizes (e.g. 100 nm × 100 nm or less).

S6. Full catalog of simulated images.

See figure caption on the final page for a description of the layout of the following simulated images:
Figure S6. Simulated images for all possible configurations having the numbers of species specified in Table S2. The first row shows an overhead view of the atomic setup used to generate the simulated images. The second row shows the corresponding positive bias images, while the third row shows negative bias. Numbers above each simulated image give the height difference between black and white for the respective image.