

## Atomically Precise Placement of Single Dopants in Si

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We demonstrate the controlled incorporation of P dopant atoms in Si(001), presenting a new path toward the creation of atomic-scale electronic devices. We present a detailed study of the interaction of  $\text{PH}_3$  with Si(001) and show that it is possible to thermally incorporate P atoms into Si(001) below the H-desorption temperature. Control over the precise spatial location at which P atoms are incorporated was achieved using STM H lithography. We demonstrate the positioning of single P atoms in Si with  $\sim 1$  nm accuracy and the creation of nanometer wide lines of incorporated P atoms.

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The ability to control the location of individual dopant atoms within a semiconductor has enormous potential for the creation of atomic-scale electronic devices, including recent proposals for quantum cellular automata [1], single electron transistors [2], and solid-state quantum computers [3]. Current techniques for controlling the spatial extent of dopant atoms in Si rely on either ion implantation techniques or dopant diffusion through optical or electron-beam patterned mask layers. While the resolution of these techniques continues to improve they have inherent resolution limits as we approach the atomic scale [4]. The work presented here looks beyond conventional techniques to position P dopant atoms with atomic precision by using scanning tunneling microscopy (STM) based lithography on H passivated Si(001) surfaces [5,6] to control the adsorption and subsequent incorporation of single P dopant atoms into the Si(001) surface.

First, we show the controlled adsorption of  $\text{PH}_3$  molecules to STM-patterned areas of H-terminated Si(001) surfaces and identify both adsorbed  $\text{PH}_3$  molecules [7] and the previously unobserved room temperature dissociation product,  $\text{PH}_2$ . We then show, using low  $\text{PH}_3$  dosed clean Si(001) surfaces, that both of these room temperature adsorbates can be completely dissociated using a critical anneal, and more importantly, that this results in the substitutional incorporation of individual P atoms into the top layer of the substrate. Finally, we combine these two results to demonstrate the spatially controlled incorporation of individual P dopant atoms into the Si(001) surface with atomic-scale precision. Of crucial importance to this final result is that the anneal temperature for P atom incorporation lies below the H-desorption temperature, so that the H-resist layer effectively blocks any surface diffusion of P atoms before their incorporation into the substrate surface.

Figures 1(a)–1(c) demonstrate the flexibility of STM H lithography to create different sized regions of bare Si(001) surface. As we will show, these regions can be used not only as a template for dopant incorporation but also to aid in fundamental studies of surface reactions. In Figs. 1(d)–1(i) we confine the adsorption of phosphine to such lithographically defined areas of bare Si in

order to identify the dissociation products  $\text{PH}_3$  and  $\text{PH}_2$ . Figure 1(d) shows a  $\sim 2$  nm wide line of exposed Si created using STM lithography on a H-terminated Si(001) surface that was subsequently dosed with 0.3 langmuir ( $L = 0.75 \times 10^{-6}$  mbar s) of  $\text{PH}_3$  gas at room

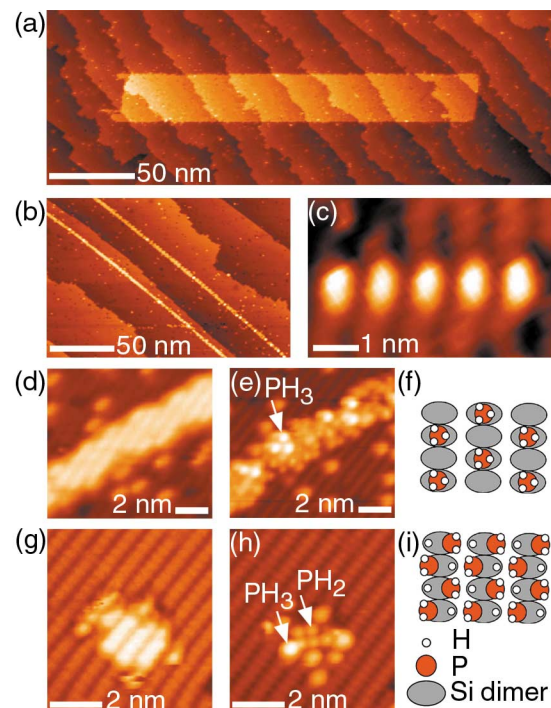


FIG. 1 (color). A STM tip has been used to remove H atoms from a H-terminated Si(001) surface to form (a)  $200 \times 30$  nm<sup>2</sup> rectangular patch, (b) two parallel lines of exposed Si(001) surface, and (c) five single H-atom desorption sites. The desorption parameters used were +4 V sample bias and 1 nA tunnel current. The areas of bare Si(001) surface appear brighter than the surrounding H-terminated surface due to the additional tunnel current contributed by the Si surface states [22]. Images (d),(g) show a  $\sim 2$  nm wide lithographic line and  $\sim 2$  nm patch of hydrogen lithography. After exposure to  $\text{PH}_3$ , the adsorbed  $\text{PH}_3$  and  $\text{PH}_2$  molecules can be seen within the lithographic areas in images (e) and (h) adsorbing with  $c(4 \times 2)$  and  $p(2 \times 2)$  periodicities, respectively, as shown in the schematics (f) and (i).

temperature [Fig. 1(e)]. Within the lithographic line in Fig. 1(e) we can identify adsorbed  $\text{PH}_3$  molecules by their appearance as circular protrusions centered on the dimer rows and ordered into a  $c(4 \times 2)$  periodicity [Fig. 1(f)] [7]. However,  $\text{PH}_3$  adsorption is known to be partially dissociative at room temperature [8], producing adsorbed  $\text{PH}_2$  and H as well as  $\text{PH}_3$ . Repeating this experiment at higher resolution using a smaller,  $\sim 2$  nm diameter patch [Figs. 1(g) and 1(h)], we have been able to identify these  $\text{PH}_2$  molecules as adsorbate protrusions positioned asymmetrically about the dimer rows [9] and ordered with a  $p(2 \times 2)$  periodicity, shown schematically in Fig. 1(i). The above results demonstrate our ability to place and identify P precursor molecules at predefined locations on a Si surface. However, to create devices with full electrical activation we need to incorporate the P atoms from these molecules into the Si surface in substitutional lattice sites.

In previous studies, Hamers and co-workers [10] suggested that individual P atoms are unstable on the Si(001) surface and substitute for surface Si atoms to form P-Si heterodimers. For this process to occur, however, the adsorbed precursor  $\text{PH}_3$  and  $\text{PH}_2$  molecules must first completely dissociate into P and H. For atomically precise placement of P in Si we require this incorporation process to take place without surface diffusion of the P atoms or desorption of the adsorbed phosphine molecules or the surrounding H-resist layer. To achieve this, we have first performed an extensive study of annealing lightly  $\text{PH}_3$  dosed clean (H-free) Si(001) surfaces. Figure 2(a) shows a STM image of a Si(001) surface that has been dosed with 0.01 L  $\text{PH}_3$ . From the results shown in Figs. 1(d)–1(i), we are able to identify molecularly adsorbed  $\text{PH}_3$  with an apparent height of  $\sim 0.07$  nm above the substrate dimer rows (our data and Ref. [11]), as well as  $\text{PH}_2$  molecules by their distinctive asymmetric bonding arrangement. Previous studies [10,12] observed the formation of P-Si heterodimers upon annealing  $\text{PH}_3$  dosed surfaces to  $\sim 550^\circ\text{C}$ . However, at this temperature all H is desorbed from the surface making this anneal temperature incompatible with H-resist lithography. Here, we use an anneal temperature of  $\sim 350^\circ\text{C}$ , which we find is sufficient to incorporate P atoms, while being below the H-desorption temperature.

The most obvious feature of the  $350^\circ\text{C}$  annealed surface, Fig. 2(b), is the appearance of bright, short, one-dimensional (1D) lines above the substrate, aligned perpendicular to the underlying dimer rows. The apparent height ( $\sim 0.14$  nm) and orientation of these 1D lines confirm that they are single dimer rows of epitaxial Si formed by the anisotropic agglomeration [13] of Si atoms ejected from the substrate. This is further evidenced by the characteristic splitting of the ejected dimer chains between filled- and empty-state tunneling conditions [14], as shown in Figs. 2(c) and 2(d).

The P-Si heterodimers in Fig. 2(b) are difficult to resolve since they are overshadowed by the very bright

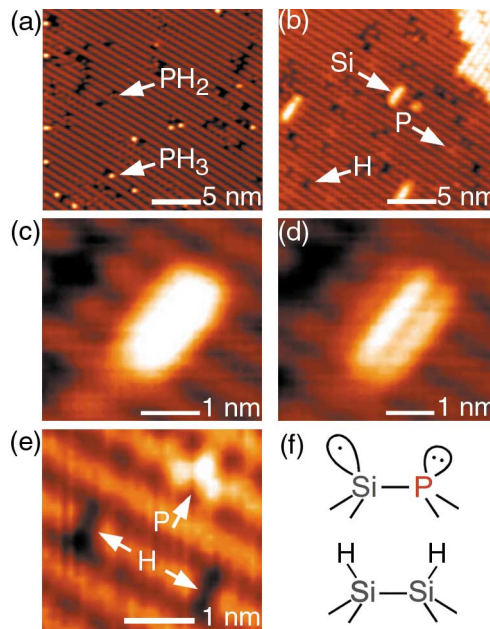


FIG. 2 (color). STM images of a  $\text{PH}_3$  dosed and annealed Si(001) surface. (a) Si(001) surface dosed with 0.01 L of  $\text{PH}_3$  gas. The  $\text{PH}_2$  molecules do not appear as bright as in Fig. 1(h) due to the additional tunnel current produced by the Si surface  $\pi$  states of the clean Si(001) surface. (b) The  $\text{PH}_3$  dosed surface after annealing to  $350^\circ\text{C}$ . (c),(d) Filled- and empty-state STM images of an ejected Si dimer chain. (e) A higher resolution image of the  $350^\circ\text{C}$  annealed surface showing a single P-Si heterodimer and two monohydride dimers. (f) Schematic diagrams of a P-Si heterodimer and a monohydride dimer. Parameters for all STM images were  $-1.6$  V and  $0.1$  nA except (d), which was imaged at  $+1.6$  V.

1D Si chains on the upper atomic layer. By examining a smaller area of the surface that is free from ejected Si, Fig. 2(e), we are able to resolve the characteristic asymmetry of the P-Si heterodimer. We measure a  $\sim 0.03$  nm height increase of the P-Si heterodimer compared to the neighboring Si dimers, which arises from the additional tunnel current due to the dangling bond of the Si atom of the P-Si heterodimer [Fig. 1(f)]. Additionally, the incorporated P atom induces static buckling of the neighboring Si dimers, such that the heterodimer appears to extend further along the dimer row than a single dimer width. The characteristic asymmetric appearance of this feature provides a clear signature of a single P atom incorporated into the Si(001) surface forming a single P-Si heterodimer.

In addition, we also observe dark, single dimer vacancylike features on the  $350^\circ\text{C}$  annealed surface [Fig. 2(e)]. These depressions are H-terminated Si dimers (monohydride, H-Si-Si-H), formed by the adsorption of H to the surface subsequent to the dissociation of the  $\text{PH}_3$  and  $\text{PH}_2$  molecules [15]. Their dark appearance in STM images is characteristic of H passivating the surface and removing the Si  $\pi$  states from the band gap.

Identification of each of the various features on the surface in Fig. 2(b) is further confirmed by STM studies of the surface at higher temperatures. Raising the anneal temperature (to  $\sim 450^\circ\text{C}$ ) causes the disappearance of the short 1D Si dimer chains from the surface as a result of the diffusion of the Si atoms from the ejected Si dimer chains to step edges, as observed in Si growth experiments [16]. Further annealing to  $\sim 550^\circ\text{C}$  results in the disappearance of the monohydride dimers, as the monohydride is desorbed from the Si(001) surface [17]. Finally, annealing to  $\sim 750^\circ\text{C}$  causes the removal of the P-Si heterodimers in agreement with the established desorption temperature of P from the Si(001) surface [18]. These studies demonstrate that P atoms can be incorporated into the Si(001) surface from adsorbed  $\text{PH}_3$  molecules by annealing to  $350^\circ\text{C}$ .

We now wish to control the spatial location of the P atom incorporation using the H-resist lithography technique. Figure 3(a) shows an STM image of a

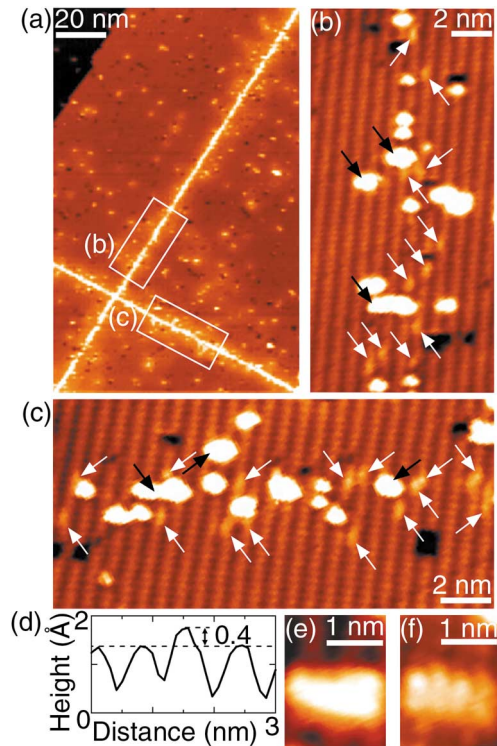


FIG. 3 (color). STM images of controlled P incorporation into Si(001) along two perpendicular  $\sim 4$  nm wide lithographic lines. (a) Lithographic lines created by moving the tip with a velocity of  $40$  nm/s while applying  $+4$  V sample bias and  $1$  nA tunnel current. (b),(c) High-resolution STM images of the boxed regions in image (a) after dosing with  $0.3$  L of  $\text{PH}_3$  and annealing to  $350^\circ\text{C}$ . Incorporated P atoms in the form of P-Si-H “hydrided heterodimers” are labeled by white arrows, while ejected Si dimer chains are labeled with black arrows. (d) Line profile taken over a single P-Si-H heterodimer, showing a  $\sim 0.04$  nm height increase due to tunneling from the P lone pair orbital. (e),(f) Filled- and empty-state STM images of a H-terminated ejected Si dimer chain.

H-terminated Si(001) surface where the STM tip has been used to selectively remove H atoms from Si along two perpendicular  $\sim 4$  nm wide lines. The patterned surface was then exposed to  $\sim 0.3$  L  $\text{PH}_3$  and annealed to  $\sim 350^\circ\text{C}$  as shown in Figs. 3(b) and 3(c). Along the length of both lithographic lines, many asymmetric features are observed, corresponding to the formation of P-Si heterodimers [indicated by white arrows in Figs. 3(b) and 3(c)]. In contrast to the clean surface results, these P-Si heterodimers are H terminated (P-Si-H) resulting from the almost complete retermination of the lithographic line with H during the  $350^\circ\text{C}$  anneal. Figure 3(d) shows a line profile taken over a single P-Si-H heterodimer, showing a  $\sim 0.04$  nm increase due to tunneling from the lone pair state of the P atom. Importantly, we find that these P-Si-H heterodimers are solely located within the  $\sim 4$  nm wide region of the original lithographic line, confirming that the H-resist layer, which survives the  $350^\circ\text{C}$  anneal intact, acts as an effective mask for the controlled incorporation of P into the surface. We also observe clear evidence of ejected Si dimer chains along (and confined to) the lithographic line. As was the case in the clean surface experiments, filled- and empty-state images of the ejected Si chains [Figs. 3(e) and 3(f)] reveal the characteristic splitting of these ejected Si dimer chains under empty-state imaging. These results demonstrate that it is possible, using an appropriate anneal, to controllably incorporate P atoms from adsorbed phosphine molecules into Si(001) at precise locations using STM-based H lithography.

We note that the  $\text{PH}_3$  dose rate and fluence is critical in obtaining the successful incorporation of P within our lithographic H-desorption sites and not at random single dimer H-desorption sites. Using both higher  $\text{PH}_3$  dose rates ( $10^{-8}$  mbar chamber pressure) and total doses ( $\sim 3$  L), we have noted the adsorption of  $\text{PH}_3$  at single H-desorption sites [19]. However, with the low dose rate and fluence used here ( $10^{-9}$  mbar and  $0.3$  L) we have observed an almost complete absence of adsorption at single H-desorption sites, with coverages approaching saturation in the larger lithographically defined desorption regions.

Finally, we have been able to achieve the ultimate limit of P atom placement in Si(001) by incorporating single P atoms into the Si(001) surface with atomic-scale precision. Figure 4(a) shows a H-terminated Si surface with a controlled desorption site of diameter  $\sim 1$  nm, exposing just two or three of the substrate Si dimers. Figure 4(b) shows the same surface area after dosing with  $\sim 0.3$  L  $\text{PH}_3$  and annealing to  $\sim 350^\circ\text{C}$ . Here we see a very clear signature of the asymmetric P-Si-H heterodimer within the  $\sim 1$  nm lithographic area and complete retermination of this area with H. This is the first demonstration of the spatially controlled incorporation of a single dopant atom in Si that can be produced repeatedly in our laboratory. In Figs. 4(c) and 4(d) we have incorporated two P atoms in Si  $\sim 12$  nm apart for the qubit array of a

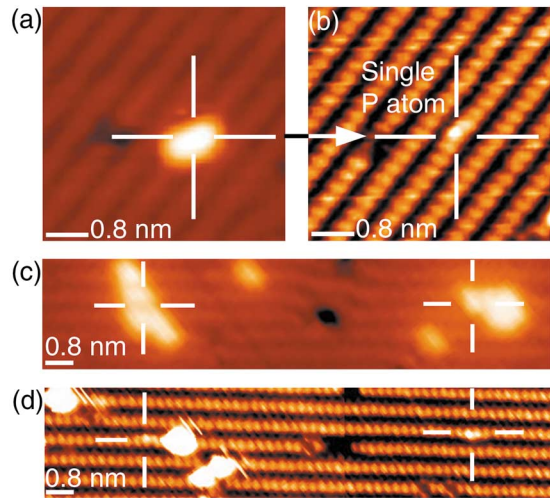


FIG. 4 (color). STM images of atomically controlled single P atom incorporation into Si(001). (a) H-terminated Si(001) with a  $\sim 1$  nm diameter H-desorption point ( $\sim 3$  dimers long). (b) The same area after  $\text{PH}_3$  dosing and annealing to  $350^\circ\text{C}$  showing a single P atom incorporated at the location defined by the H-desorption point. (c) Two H-desorption sites separated by  $\sim 12$  nm. (d) The same area of the surface shown in (c), after  $\text{PH}_3$  dosing and annealing to  $350^\circ\text{C}$ . A single P atom has been incorporated into the surface within both of the two lithographically defined areas. The separation of these two P atoms ( $\sim 12$  nm) is of the order of the 20 nm separation required for the P qubit array of the Kane solid-state quantum computer [3].

Si-based quantum computer [3]. Figure 4(c) shows two desorption sites of diameter  $\sim 1$  nm and separated by  $\sim 12$  nm. After  $\text{PH}_3$  dosing and annealing we observe the incorporation of a single P atom at each of these lithographic sites, as seen in Fig. 4(d). We note the presence of two single H atom desorption sites in addition to the two lithographically defined desorption regions in Fig. 4(c). However, as seen in Fig. 4(d), these sites do not produce incorporated P atoms at the low  $\text{PH}_3$  dose rate and fluence used. Additionally, in Fig. 4(d), several single H atom desorption sites are seen as white protrusions surrounding the left P-Si-H heterodimer. These are the result of single H atom desorption events during the  $350^\circ\text{C}$  anneal and do not affect the P atom placement. The  $\sim 1$  nm placement accuracy that we demonstrate here is more than adequate for the Kane qubit architecture [3].

In summary, we have demonstrated the first controlled incorporation of single P dopant atoms in Si with atomic-scale precision. To elucidate this, we have first studied the interaction of  $\text{PH}_3$  with the Si(001) surface and, in particular, observed the substitutional incorporation of P atoms into the substrate after annealing to  $350^\circ\text{C}$ . We then employed STM-based H lithography to control the spatial locations of P atoms incorporated into the substrate. Critical to this result is that the  $350^\circ\text{C}$  anneal lies well below the H-desorption temperature such that

the H-resist layer acts as an atomic-scale mask for controlled P atom incorporation. Preliminary studies to encapsulate these dopants in Si — and observe the resulting change in surface electrostatic potential [20] to confirm minimal segregation of array — are underway with promising results [21]. These results open the door to the exciting possibility of creating electronic devices in Si with atomically controlled dopant profiles.

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