Atomic-control placement of individual P atoms in Si for the fabrication of a quantum computer qubit array

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ABSTRACT

Controlling the location of individual dopant atoms in silicon has great potential for the creation of atomic-scale electronic devices, such as the solid-state quantum computer proposed by Kane [*Nature* 14 May 1998]. We demonstrate the incorporation of phosphorus atoms into a Si substrate at spatial locations controlled with atomic-precision using a scanning tunneling microscope (STM). A hydrogen monolayer was used as a lithographic resist that was patterned by desorbing H from the surface using an STM tip. Phosphine molecules were then adsorbed to the exposed areas of bare Si surface, and subsequently P atoms from these adsorbates were incorporated into the Si surface by performing a critical anneal to $\sim 350°C$. Using this technique we demonstrate the controlled incorporation of P atoms into Si with a positional accuracy of order 1 nm. These results represent the first demonstration of controlled single dopant atom incorporation in Si at the atomic-scale.

Keywords: Silicon, Lithography, STM, Nanoelectronics, Doping

1 Atomic-scale electronic devices

While the size of electronic components in integrated circuits has been steadily decreasing for decades, this trend cannot continue at the same pace indefinitely using current technologies such as optical lithography [1]. Indeed, a lot of fundamental research is being conducted into new technologies to fabricate nanometer-size features, including Si nanoimprinting [2], the creation of semiconductor nanowire [3] and carbon nanotubes devices [4], and single-atom transistors [5]. In addition to facilitating the continued miniaturization of conventional semiconductor devices, such new technologies also promise the creation atomic-scale devices for the exploitation of quantum effects, such as quantum cellular automata [6]. One of the most ambitious proposals for such a device is the solid-state quantum computer proposed by Kane [7], which requires the fabrication of a regularly-spaced array of individual P atoms as qubits, ~ 20 nm apart in a Si substrate. Here, we demonstrate the controlled incorporation of P dopant atoms in Si with atomic-scale precision, presenting a new path toward the creation atomic-scale devices, and in particular toward the creation of the P qubit array of a solid-state quantum computer. We use the tip of a scanning tunnelling microscope to remove individual H atoms from a H monolayer covering a Si (001) surface. This H monolayer then acts as a lithographic resist-, or mask-layer for the incorporation of P atoms into the Si substrate with a positional accuracy of order 1 nm.

2 Controlled phosphine (PH_3) adsorption on silicon

We have undertaken a series of P doping studies in Si using phosphine (PH_3) gas as the dopant source and Si substrates orientated in the (001) direction. The interaction of PH_3 with the Si (001) surface and its temperature dependent behavior have been the subject of many studies over the past two decades [8]–[11], largely due to the standard use of both Si (001) and PH_3 in the semiconductor industry. However, at the atomic-scale the interaction of PH_3 with Si (001) is still not completely understood. Using H-lithography to control the spatial extent of the reaction of PH_3 with the Si (001) surface, we have been able to gain new insight into the nature of this interaction at the atomic-scale. In particular, we have unambiguously identified PH_3 and PH_2 molecules adsorbed to the Si (001) surface, and describe the process of controlled P incorporation into the silicon substrate.

Figure 1 shows the results of an investigation into the adsorption of PH_3 to the Si (001) surface. Figure 1a shows a Si (001) surface that has been chemically passivated with a monolayer of atomic H by exposure to ~ 140 L (L = Langmuir = 10^{-6} torr s) of H_2 gas passed over a $\sim 1500°C$ tungsten filament. Subsequently, a large rectangular patch ($\sim 300 \times 50$ nm^2) of bare Si (001) surface has been exposed by desorbing the H from this region using the STM tip [12]. The patch of bare Si (001) surface appears brighter in the STM image due to the additional STM tunnel current that arises from the Si surface π-states [13]. This surface was then exposed to a sub-saturation dose of PH_3 gas (0.23 L), and a section of this surface (corresponding to the boxed region in Fig. 1a) is shown in Fig. 1b. This image shows phosphine species which uniformly cover the area within the

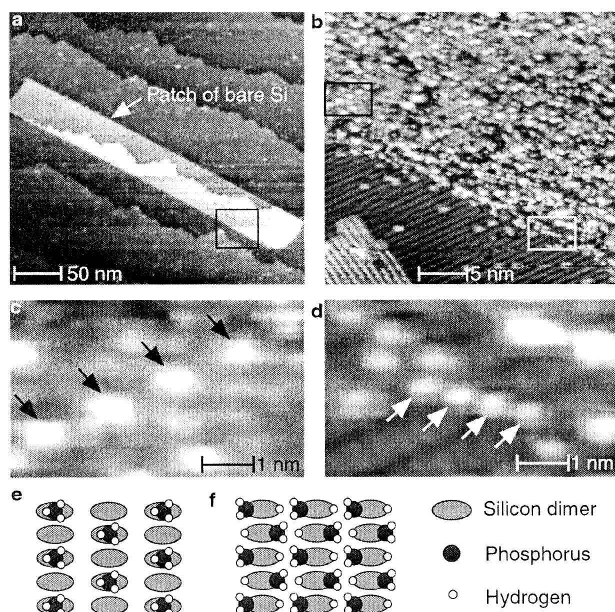

Figure 1: A STM tip with –4 V tip voltage and 1 nA tunnel current was used to controllably desorb H from a H-terminated Si (001) surface, which was subsequently dosed with phosphine gas. The desorbed area (a) is a 300×50 nm^2 rectangular patch. The image (b) corresponds to the boxed area in (a), subsequent to the surface being dosed with PH_3 gas. Adsorbed PH_3 and PH_2 molecules can be identified within the lithographic patch: (c) shows the black boxed area of (b) where four PH_3 molecules (black arrows) can be seen ordering onto every other dimer along a dimer row with a $c(4 \times 2)$ periodicity. (d) shows the white-boxed area of (b) where four PH_2 molecules (white arrows) can be seen ordering onto alternating sides of dimer rows with a $p(2 \times 2)$ periodicity. Schematic diagrams show (e) PH_3 molecules adsorbed with $c(4 \times 2)$ periodicity and (f) PH_2 adsorbed with $p(2 \times 2)$ periodicity.

lithographic patch. The surrounding H-terminated surface remains free from adsorbates, demonstrating the effectiveness of the H layer as a lithographic resist for the adsorption of PH_3, as previously reported [14].

In Fig. 1b we can simultaneously observe the PH_3 dosed area of the Si (001) surface within the lithographic patch, and can compare its topography with the surrounding H-terminated surface (in which the periodicity of the underlying substrate can be identified). Both the clean and monolayer-H-terminated Si (001) surfaces consist of rows of paired Si atoms called dimers, giving a 2×1 periodicity, as observed in the H-terminated region in Fig. 1b. However, within the lithographic patch these rows of dimers have been replaced by bright circular protrusions of the adsorbed molecules. Close observation of these adsorbates reveals that they come in two characteristic sizes and order with two different periodicities. Using the H-terminated surface as a reference it is possible to see that the larger of the two adsorbate protrusions are found centered over the substrate dimer rows and order onto every other dimer along a dimer row. Four such molecules are shown in Fig. 1c. We readily identify these as PH_3 molecularly adsorbed in the on-top position of the Si dimers with a $c(4 \times 2)$ periodicity, as previously reported by Hamers *et al.* [15] and shown schematically in Fig. 1e. In contrast, the smaller of two adsorbate protrusions are found on one side of a dimer row and exhibit ordering into a $p(2 \times 2)$ periodicity, as can be clearly seen in Fig. 1d. We attribute these protrusions to be adsorbed molecules that have undergone a spontaneous dissociation to PH_2 and H, adsorbed to opposite sides of a single surface dimer as recently predicted from first-principles calculations [16]. The adsorbed PH_2 molecules order by bonding to opposite sides of the Si dimers for adjacent dimers along a dimer row, giving rise to a $p(2 \times 2)$ periodicity, as shown schematically in Fig. 1(f). While it has long been known that the adsorption of PH_3 to the Si (001) surface is partly dissociative [17] (both PH_3 and PH_2 species are present on room temperature dosed surfaces), this is the first direct observation of PH_2 molecules on the Si (001) surface. Finally, we note that while the PH_2 molecules are observed as protrusions with respect to the H-terminated Si (001) surface, the additional current that arises from the π-states of the clean surface means that PH_2 molecules do not protrude significantly from the clean Si (001) surface (in STM images). This fact provides an explanation why PH_2 adsorbates have gone unidentified until now.

3 Lithographically controlled P incorporation into Si (001)

The studies presented so far have demonstrated that H-lithography can be used to control the spatial positions of PH_3 and PH_2 adsorbates on Si (001). However, our goal is to demonstrate a process for creating an atomic array of P atoms in Si to form the qubit array of a solid state quantum computer. We therefore turn our attention to the controlled incorporation of P atoms in lithographically defined regions in a H-terminated Si (001) surface.

Figure 2 shows the results of PH_3 dosing and thermally annealing a ~ 4 nm wide lithographic line in a H-terminated Si (001) surface. This line spans two substrate terraces and therefore runs perpendicular to the substrate dimer rows for half of its length and parallel for the other half. Two sections of the line, one from each terrace, are shown in Figs. 2a and 2c. The corresponding areas of the surface after dosing with 0.23 L PH_3 and annealing to 350°C are shown in Figs. 2b and 2d. From these images it is apparent that much of the

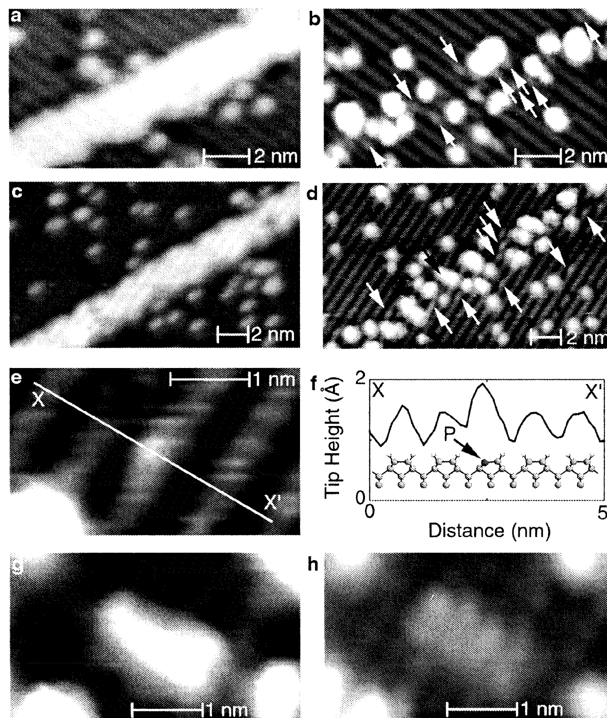

Figure 2: Phosphorus atoms controllably incorporated into Si (001) along a ∼ 4 nm wide line. Images in (a) and (c) show sections of the lithographic desorption line taken from two separate substrate terraces, while (b) and (d) show the corresponding regions of the surface subsequent to PH_3 dosing and annealing to ∼ 350°C. A single P-Si-H heterodimer is shown in (e) with the corresponding line profile give in (f). A high resolution image of a single ejected Si dimer chain is given in (g) and the corresponding empty-state STM image of the ejected dimer chain shown in (h). Note the characteristic splitting of the ejected Si dimer chain and the substrate dimers into pairs of protrusions in the empty-state image.

area contained within the lithographic lines becomes reterminated with H after PH_3 dosing and annealing. The extra H adsorbed to these areas is generated by the dissociation of the adsorbed PH_3 and PH_2 molecules, which are known to completely dissociate on Si (001) at temperatures above ∼ 300 °C [8], [17], [18].

We might also expect to find individual P atoms adsorbed to the surface within the lithographic lines. However, it has been shown that individual P atoms are unstable on the Si (001) surface and substitutionally incorporate into the surface to form P-Si heterodimers [15], [19]. Such P-Si heterodimers appear as asymmetric protrusions in the surface. Close examination of Figs. 2b and 2d reveal the presence of these asymmetric Si-P heterodimers along the entire length of, and confined to the areas of both lithographic lines, as indicated by white arrows. One of these P-Si heterodimers is shown in more detail in Fig. 2e. The corresponding line profile, Fig. 2f, reveals that the protrusion of this P-Si heterodimer extends ∼ 0.04 nm above, and has a shoulder that is the same height as the surrounding H-terminated Si dimers. These observations strongly suggest the P-Si heterodimers are H-terminated (P-Si-H), as indicated schematically in Fig. 2f, and the protrusion of the heterodimer can be attributed to tunneling from the lone pair orbital of the P atom.

However, an important question remains to be answered: since the incorporation of P atoms into the surface necessarily involves the displacement of Si atoms from the surface, where are these displaced Si atoms? The majority of the bright (white) features [20] that can be seen in Figs. 2b and 2d are bare Si dimers. However, we have observed a number of protrusions along the lithographic line that appear as short one-dimensional (1D) lines, orientated perpendicular to the underlying substrate dimer rows, as indicated with a black arrow in Fig. 2d and shown in more detail in Fig. 2g. These 1D features have an apparent height of ∼ 0.14 nn and exhibit splitting into pairs of lines when imaged with empty-state tunneling conditions, Fig. 2h. The characteristics of these 1D lines confirm that they are short chains of Si dimers on top of the substrate, which have formed due to the anisotropic agglomeration [21] of Si atoms on the surface as a result of their displacement from the substrate by P atom incorporation.

In summary, we have used STM-based H-lithography to control the spatial extent of P atoms incorporated into the Si (001) substrate. In the first stage of our experiments, we used a H-resist layer on a Si (001) surface to control the spatial extent of the adsorption of PH_3 to the surface. These results allowed us to determine the appearance of both PH_3 and PH_2 on the exposed Si (001) surface. Subsequent annealing of these surfaces resulted in the controlled incorporation of P atoms into Si at precise lithographic locations. This was confirmed by the direct observation of incorporated P-Si-H heterodimers, the re-adsorption of H and the ejection of Si from the surface. Using this technique we have created a single ∼ 4 nm line of P dopants in the Si (001) surface, constituting the first demonstration of dopant atom incorporation in Si with atomic-precision. Experiments are currently underway to refine this technique to incorporate single P atoms in the Si (001) surface with a separation of ∼ 20 nm, as required for the qubit array of the Kane quantum computer.

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