STM characterization of the Si-P heterodimer

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We use scanning tunneling microscopy (STM) and Auger electron spectroscopy to study the behavior of adsorbed phosphine (PH$_3$) on Si(001), as a function of annealing temperature, paying particular attention to the formation of the Si-P heterodimer. Dosing the Si(001) surface with ~0.002 Langmuirs of PH$_3$ results in the adsorption of PH$_x$ (x=2,3) onto the surface and some etching of Si to form individual Si ad-dimers. Annealing to 350°C results in the incorporation of P into the surface layer to form Si-P heterodimers and the formation of short 1-dimensional Si dimer chains and monohydrides. In filled state STM images, isolated Si-P heterodimers appear as zig-zag features on the surface due to the static dimer buckling induced by the heterodimer. In the presence of a moderate coverage of monohydrides this static buckling is lifted, rendering the Si-P heterodimers invisible in filled state images. However, we find that we can image the heterodimer at all H coverages using empty state imaging. The ability to identify single P atoms incorporated into Si(001) will be invaluable in the development of nanoscale electronic devices based on controlled atomic-scale doping of Si.

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I. INTRODUCTION

Currently there are several proposals to use phosphine gas (PH$_3$) to create atomic-scale devices by positioning P atoms on a surface using H-lithography. One such idea involves the fabrication of a 2-dimensional array of P atoms in Si for the realization of a silicon based quantum computer. A requirement of each of these schemes is that the P atoms, re unhindered the PH$_3$ molecules, are incorporated into substitutional lattice sites. Since PH$_3$ is used for doping Si in the semiconductor industry, the interaction of PH$_3$ with the Si(001) surface has been studied for over two decades using a wide variety of surface sensitive techniques (e.g., Ref. 1). It is well established that the adsorption of PH$_3$ on the Si(001) surface is partially dissociative, resulting in the adsorption of both PH$_3$ and PH$_2$. Moreover, it is known that annealing PH$_3$ dosed surfaces causes the complete dissociation of the adsorbed PH$_3$ and PH$_2$ molecules (estimates of the temperature at which this occurs vary within the range 300°C - 425°C). The majority of the investigations mentioned above have studied the interaction of phosphine with the Si(001) surface at high surface coverages. However, at low coverages there are only two papers reporting detailed atomic-resolution scanning tunneling microscopy (STM) investigations of the Si(001):PH$_3$ system, the first by Wang et al. and the second by Kipp et al. While the experimental results presented in these two papers are in good agreement, their interpretations are contradictory.

The experimental results from Wang et al. and Kipp et al. showed that after the Si(001) surface was exposed to a low dose of PH$_3$, two types of bright features appeared on the surface. Both features were centered on top of the Si dimer rows, with one feature larger than the other. Wang et al. also observed an increase in the number of dimer vacancies on the surface after PH$_3$ dosing. In both studies, after the dosed surfaces were annealed (to 230°C, Ref. 14 and to 350°C, Ref. 15), the two types of bright feature disappeared from the surface and were replaced by 1-dimensional (1-D) chains running perpendicular to the underlying Si dimer rows and a few small 2-dimensional (2-D) islands. The above data was interpreted by Wang et al. in the following way: the larger bright feature was a single Si atom (a monomer) ejected from the surface and the smaller bright feature was a PH$_3$ molecule adsorbed on top of a Si dimer. Upon heating the surface to 230°C the Si monomers combined to form 1-D rows and small 2-D islands. This annealing also induced complete PH$_3$ dissociation, with the P atoms being incorporated into the surface and the H adsorbed onto the surface to form monohydride dimers. Kipp et al. presented a different interpretation of the above data. They concluded that the large bright features were PH$_n$ (n=1-3) molecules adsorbed at defects and the small bright features were P-P dimers, resulting from the pairing and subsequent dissociation of two PH$_3$ molecules (with the dissociated hydrogen atoms also bonding to the surface). Upon heating the surface to 350°C Kipp et al. concluded that the P-P dimers coalesce to form small chains and islands. They suggested that the formation of large islands was hindered by the presence of adsorbed H on the surface.

In contrast to the results of Wang et al. and Kipp et al., separate Fourier transform infrared spectroscopy studies and a combined electron energy loss spectroscopy and thermal programmed desorption studies have indicated that molecular PH$_3$ adsorption is accompanied by a partial dissociation of PH$_3$ to form adsorbed PH$_2$ and H, during phosphine adsorption at room temperature. Therefore, further study of this system is required to consolidate the different interpretations. We have used
high resolution STM and Auger electron spectroscopy to study the evolution of a PH$_3$ dosed Si(001) surface, as a function of temperature and coverage. Particular emphasis was placed on the process of P incorporation into the Si(001) surface and the formation of the Si-P heterodimer. To this end we have also performed a study of surface segregated P from a Si encapsulated δ-doped layer. Pivotal to these experiments is the ability to resolve the presence of a single P atom in the Si(001) surface using STM. We show that the isolated Si-P heterodimer appears as a zig-zag feature in filled state STM images, but that the heterodimer is not visible if there is a moderate coverage of monohydrides on the surface. However, empty state imaging can be used to identify the heterodimers at all coverages.

II. EXPERIMENTAL

Experiments were performed in ultra-high vacuum (base pressure < 5 × 10$^{-11}$ mbar) using an Omicron variable temperature STM and electrochemically etched tungsten tips. The n-type Si(001) sample had a resistivity of ∼ 1 Ωcm and was prepared in vacuum by out-gassing overnight at 575°C using a resistive heater element, followed by flashing to 1175°C by passing a direct current through the sample. After flashing, the samples were cooled slowly (∼3°C/s) from 900°C to room temperature. For all anneal steps the sample temperature was maintained at the stated anneal temperature for 10 seconds unless stated otherwise. The PH$_3$ dosing was performed by opening a precision leak valve, which faced the chamber with a 1 mbar pressure of PH$_3$ and controlling the dose in Langmuirs (1 L = 10$^{-6}$ Torr pressure) via the dose time. The ionization gauge was not in line-of-sight of the sample. All STM images were taken at room temperature and are filled state images taken with a Dual bias STM where filled and empty state images are obtained simultaneously, were taken with a 1 nm × 17 nm area of a Si(001) surface before and after dosing with 0.002 L of PH$_3$, respectively. The circled features in (a) are single dimer vacancy defects which are inherent to the clean surface and which we identify to distinguish them from species resulting from PH$_3$ dosing. After PH$_3$ dosing [Fig. 1(b)] we find that additional features have appeared on the surface, which are: (i) adsorbed PH$_3$, (ii) adsorbed PH$_2$ + H, (iii) dimer vacancies (in addition to those present before dosing) and (iv) Si ad-dimers. Figure 1(c) shows an image of a PH$_3$ molecule which has a height/diameter of 0.9 Å/11 Å in filled state images and is adsorbed upon the center of a dimer row, as previously identified by Wang, Shan and coworkers. It can be seen in Fig. 1(c) that this molecule is adsorbed adjacent to a defect, which we find is commonly the case at low coverage. We believe that defects stabilize the adsorption of the PH$_3$ molecules centered over Si dimers. However we cannot rule out the possibility that the feature is a PH$_2$ radical centered on the dimer row, as suggested by Lin et al. Figure 1(d) shows a PH$_3$ molecule after it has dissociated into PH$_2$ + H on a single Si dimer, as described. The observation of both adsorbed PH$_3$ in its molecular form, and as the dissociation products PH$_2$ + H is in agreement with FTIR and photoemission results.

The third type of features in Figure 1(b) are single and multiple dimer vacancies, resulting directly from the removal of Si from the surface layer during PH$_3$ dosing. While dimer vacancies are difficult to distinguish from
monohydride dimers (formed when each Si atom of a dimer is terminated with an H atom) the formation of monohydride dimers is not expected at room temperature since single H atoms have insufficient mobility to diffuse and pair-up into monohydrides.\cite{Note10} We assign the fourth feature to be a Si ad-dimer, centered on the dimer rows with a height/diameter of 1.3 Å/13 Å in the filled state image and a height/diameter of 1.9 Å/13 Å in the empty state, in agreement with the observation of Si ad-dimers by Swartzentruber\cite{Note11} and shown in Fig. 2(c) and (f) respectively. The filled state height of the feature (1.3 Å) is of the same order as the distance between [001] planes of the Si crystal (1.36 Å) as expected for a Si ad-dimer. We discount the suggestion of Wang \textit{et al.}\cite{Note12} that the feature is a Si monomer, since Si monomers are not observed in filled state images.\cite{Note10} We also rule out the fourth feature being either adsorbed P or PH species because Fourier transform infrared spectroscopy\cite{Note10} and photoemission\cite{Note10} results show that these species are not formed after room temperature PH$_3$ adsorption on Si(001).

\section*{B. P identification using STM and AES}

We now describe the incorporation of P atoms into the surface, to form Si-P heterodimers, upon annealing. Fig. 2(a) shows a Si(001) surface that has been exposed to 0.002 L of PH$_3$ and annealed to 350°C. Three distinct types of feature are present on the surface, Si-P heterodimers, ejected Si dimer chains and monohydride dimers. The ejected Si chains appear as short bright lines running perpendicular to the dimer rows. These features have the same height above the surface (1.36 Å) as a monolayer Si step\cite{Note13} and have a characteristic minima running lengthways along their center in empty state images (see Fig. 4(d)), indicating that they are indeed Si dimer chains as suggested by Wang \textit{et al.}\cite{Note14} and not P dimer chains as proposed by Kipp \textit{et al.}\cite{Note15} The monohydride dimers (H-Si-Si-H) appear as dark features, similar in appearance to missing dimer defects. Fig. 2(b) shows a high resolution image of two Si-P heterodimers, which appear as zig-zags along the dimer row, with the highest part ≈ 0.3 Å above the surface dimers.\cite{Note16} This zig-zag appearance indicates there is static buckling of the surface dimers on either side of the Si-P heterodimer. Figure 2(b) shows that this buckling decays in amplitude as a function of distance from the Si-P heterodimer and extends 2-3 dimers away from it.

To confirm the interpretation of Fig. 2(a) presented above, we compare the number of Si-P heterodimers in STM images with the fraction of P at the surface measured by Auger electron spectroscopy (AES). In order to control the number of Si-P heterodimers at the surface without the complication of ejected Si dimer chains and adsorbed H (Fig. 2(a)), we have created a buried P δ-doped layer and then diffused varying amounts of the P atoms to the surface using a range of anneal tempera-

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{fig2.png}
\caption{(a), (b) STM images of a Si(001) surface after dosing with 0.002 L of PH$_3$ and annealing to 350°C at low and high resolution respectively. (c),(d) STM images of a Si(001) surface after saturation dosing with PH$_3$, annealing to 600°C, overgrowing with 5 ML of Si at room temperature and then annealing to (c) 450°C and (d) 600°C. (e) Auger electron spectra obtained from the surfaces shown in (c) and (d).}
\end{figure}
conclude, following Wang et al., that the processes that occur as a result of the 350°C anneal are as follows; the PH\textsubscript{x} (x=2,3) molecules firstly undergo complete dissociation. Each P atom then undergoes a substitution reaction with one atom of the Si surface dimer to form a Si-P heterodimer in the plane of the surface, thereby ejecting the displaced Si atom onto the surface. At 350°C the displaced Si atoms are mobile enough to diffuse short distances\textsuperscript{22} and subsequently form 1-D dimer chains on the surface. The H atoms liberated from PH\textsubscript{x} dissociation are highly mobile at 350°C and pair up to form the energetically favorable monohydride dimers\textsuperscript{22}.

C. The changing appearance of the Si-P heterodimer with coverage

We have found that the appearance of the Si-P heterodimer varies greatly as a function of initial PH\textsubscript{3} coverage. Figure 3 shows a Si(001) surface after exposure to 2 different doses (0.002 L and 0.01 L) of PH\textsubscript{3} and subsequent annealing of the dosed surfaces to 350°C and then 500°C. If we compare the two 350°C anneals, Fig. 3(a) and (b), we see that the surface that was exposed to the higher PH\textsubscript{3} dose has significantly more Si chains and the onset of 2D Si island formation (Fig. 3(b)), as expected. After both the lower and higher dosed surfaces have been subject to a further anneal of 500°C the Si chains have now disappeared, see Fig. 3(c) and (d). This can be explained since at 500°C the diffusion of Si atoms on the surface is sufficient that all the Si ad-dimers migrate to step edges to which they preferentially bond. We now consider what information we can determine about the Si-P heterodimers, from Fig. 3. If we just consider Fig. 3(c) and 3(d), which show the lower and higher dosed surfaces after annealing to 500°C, the data fits our explanation of the evolution of the PH\textsubscript{3} dosed Si(001) surface i.e. the more PH\textsubscript{x} (x=2,3) initially adsorbed on the surface, the more Si-P heterodimers are observed on the surface after the 500°C anneal. However, the 350°C anneals of the lower and higher dosed surfaces are not so easy to understand. We repeatedly observe that lower dosed, 350°C annealed surfaces such as that of Fig. 3(a) show moderate densities of Si-P heterodimers and monohydrides, as expected. Conversely, the higher dosed, 350°C annealed surfaces such as that of Fig. 3(b) appear to show a high density of monohydrides and no Si-P heterodimers. We know from the 500°C anneal of the higher dosed surfaces that Si-P heterodimers are abundant, so we can conclude that a high density of monohydrides inhibits the observation of Si-P heterodimers with the STM. It is known that monohydride dimers exhibit very little buckling\textsuperscript{22} and thus pin neighboring Si dimers in an unbuckled geometry. Hence, if the density of monohydrides is sufficiently high it is reasonable to assume that almost all the surface Si dimers are pinned, even those in the vicinity of Si-P heterodimers. As a consequence, the characteristic zig-zag appearance of the Si-P heterodimer will be suppressed. It is now interesting to look again at Fig. 3(d) which was obtained by annealing a buried P layer (with no H present) to 600°C. Whilst a sufficient number of P atoms have diffused to the surface to yield a high density of Si-P heterodimers, the surface is free of H. In this image the Si-P heterodimers are clearly visible, which is consistent with the observation that it is a high density of monohydrides on the surface that inhibits the STM observation of Si-P heterodimers.

Our final anneal of the PH\textsubscript{3}/Si(001) low dosed surface (not shown) was performed at 700°C and resulted in the disappearance of the Si-P heterodimers. By comparing our results with that from the annealing of a saturation dosed PH\textsubscript{3}/Si(001) surface\textsuperscript{16} we conclude that the P atoms have desorbed from the surface, leaving only features inherent to the clean Si(001) surface.

D. Identification of the Si-P heterodimer using empty state imaging

In the previous section we showed that for high coverages of monohydrides, the identification of Si-P heterodimers in filled state images was not possible. However, we will show that we can clearly identify Si-P heterodimers, at any coverage, using empty state imaging. Figure 4 shows (a) filled- and (b) empty-state images of the same area of a Si(001) sample after a 0.002 L PH\textsubscript{3} dose and a 500°C anneal. We have chosen a low PH\textsubscript{3} dose.
and an anneal temperature sufficiently high that ejected Si dimer chains and monohydrides have been completely removed from the surface, so that we can image Si-P heterodimers in isolation from other features. Figure 4(b) shows that in empty state images the Si-P heterodimer appears as a bright circular protrusion on one side of a dimer row with a slight depression on the other side of the row. The height of the protrusion, measured with respect to the surface dimers, varies linearly with bias between $0.50 \pm 0.05$ Å at $+0.8$ V to $0.10 \pm 0.02$ Å at $+2.0$ V. Dimer buckling in empty state images of Si(001) is not observed for sample biases greater than $+0.8$ V.\(^\text{14,17}\)

With the Si-P heterodimer well characterized in both filled and empty state imaging we can now also interpret images obtained after higher PH$_3$ doses but a lower anneal temperature, where H is still present. Figures 4(c) and (d) are dual bias images of a Si(001) surface that has been dosed with 0.013 L of PH$_3$ and annealed to 350°C. The filled state image shows a number of Si chains and monohydrides but no Si-P heterodimers are observed. We see that the ejected Si chains have a characteristic minima running lengthways along their center in the empty state image, as expected.\(^\text{14,17}\) However, despite the difficulty in resolving features due to the extreme brightness of the ejected Si, in the empty state image we still see circular protrusions characteristic of the Si-P heterodimers, as well as the Si chains and the monohydrides. This ability to identify incorporated P atoms regardless of the density of other features on the surface is a useful tool for locating P atoms in Si, towards the goal of realizing atomic-scale devices.\(^\text{1,3}\)

IV. CONCLUSION

We have used scanning tunneling microscopy (STM) and Auger electron spectroscopy (AES) to study the incorporation of P into Si(001) by dosing with small quantities of PH$_3$ and annealing. The Si-P heterodimer appears as a zig-zag feature when imaged in filled state STM images due to the static dimer buckling induced by the heterodimer. The Si-P assignment was confirmed from the direct correlation between the number of zig-zag features imaged by STM and the fraction of P at the surface measured by AES. The presence of moderate numbers of monohydrides on the surface removes the buckling induced by the Si-P heterodimer and renders the heterodimer invisible in filled state images. We characterized the Si-P heterodimer using empty state imaging and show that, in the empty state the Si-P heterodimers are visible even with a high coverage of monohydrides. The demonstration of the incorporation of individual P atoms into the Si(001) surface, and subsequent characterization using STM, is an important step towards fabrication of nanoscale electronic devices based on controlled atomic-scale doping of Si.

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