The Adsorption and Thermal Decomposition of PH$_3$ on Si(111)-(7x7)

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The Adsorption and Thermal Decomposition of PH$_3$ on Si(111)-(7×7)


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Phosphine
Phosphorus, Hydrogen, Phosphide, Surface Science Center

The adsorption of PH$_3$ on Si(111)-(7×7) has been studied by Auger electron spectroscopy and temperature programmed desorption. PH$_3$ was found to exhibit two kinds of behavior on the surface. A small surface coverage of molecularly adsorbed PH$_3$ desorbs without any dissociative surface chemistry. For the majority of the adsorbed PH$_3$ species (2x2) dissociation occurs to form P(a) and H(a). At 120 K, PH$_3$ initially adsorbs as the reactive species with a sticking coefficient of ~1 up to 75% saturation. The reactive PH$_3$ species surface concentration saturates at 1.8x10$^{14}$ PH$_3$ cm$^{-2}$. Surface H(a), produced by PH$_4$ thermal decomposition, desorbs as H$_2$(g) at T>700 K, and P(a) desorbs as P$_2$(g) at T>900 K. Capping the Si-dangling bonds with atomic hydrogen prevents PH$_3$ adsorption, indicating that the dangling bonds are the PH$_3$ adsorption sites. Isotopic studies involving Si-D surface species mixed with adsorbed PH$_3$ species indicate that PH$_3$ desorption does not occur through a recombination process. Finally, additional PH$_3$ may be adsorbed if the surface hydrogen produced by dissociation of PH$_3$ is removed. Evidence for P penetration into bulk Si(111) at 875 K is presented.
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Abstract

The adsorption of PH₃ on Si(111)-(7x7) has been studied by Auger electron spectroscopy and temperature programmed desorption. PH₃ was found to exhibit two kinds of behavior on the surface. A small surface coverage of molecularly adsorbed PH₃ desorbs without any dissociative surface chemistry. For the majority of the adsorbed PHₓ species (3≥x≥1) dissociation occurs to form P(a) and H(a). At 120 K, PH₃ initially adsorbs as the reactive species with a sticking coefficient of S=1 up to ~75% saturation. The reactive PHₓ species surface concentration saturates at 1.9±0.3x10¹⁴ PHₓ cm⁻². Surface H(a), produced by PHₓ thermal decomposition, desorbs as H₂(g) at T>700 K, and P(a) desorbs as P₂(g) at T>900 K. Capping the Si-dangling bonds with atomic deuterium prevents PH₃ adsorption, indicating that the dangling bonds are the PH₃ adsorption sites. Isotopic studies involving Si-D surface species mixed with adsorbed PHₓ species indicate that PH₃ desorption does not occur through a recombination process. Finally, additional PH₃ may be adsorbed if the surface hydrogen produced by dissociation of PH₃ is removed. Evidence for P penetration into bulk Si(111) at 875 K is presented.
I. Introduction

In the doping of silicon, phosphorus is often incorporated substitutionally to create a localized electron state below the conduction band. The phosphorus may be incorporated into the silicon lattice by either ion implantation of P⁺ [1-4], or chemically using phosphorus-containing molecules added during the growth of silicon films [5-11]. The use of phosphine, PH₃, to dope films of a-Si:H with phosphorus during chemical vapor deposition (CVD) from silane has been shown to be effective [5-8; 10-12]. In these studies, however, a dramatic decrease in silicon deposition rate was observed, as compared to growth without phosphine, suggesting that species on the Si surface produced from PH₃ retard the surface decomposition of silane [5,6,10,12].

The adsorption of phosphine on Si(100) and its effects on the co-adsorption of silane has been studied by Yu and Meyerson [12]. They report that PH₃ "mostly adsorbs non-dissociatively" [13] with an initial sticking coefficient of \(S₀=1.0\) at room temperature, compared to \(S₀=0.0015\) for silane [12]. The adsorbed phosphine was reported to decompose at temperatures near 475 K into 3(Si-H) and Si-P [13]. At a temperature of 675 K, SIMS measurements indicate the desorption of surface hydrogen [12]. The desorption of hydrogen opens up silicon sites where further phosphine adsorption may take place. At temperatures above 875 K, surface phosphorus was depleted, as measured by Auger electron spectroscopy [12], leaving a clean silicon surface. Desorption of P₂ was later reported [13] in thermal desorption studies with an onset temperature of ~875 K and a peak maximum at ~975 K.

Van Bommel and Meyer [11] have reported a low energy electron diffraction (LEED) study of phosphine adsorption on Si(111) as a function of both surface temperature and phosphine pressure. The pressure vs temperature phase diagram
has seven different P-Si phases. The phosphine adsorbed at room temperature formed a P-(7x7) phase, stable to temperatures below 770 K, later shown to have 0.33 P/Si [14]. At a phosphine pressure of 10^{-7} Torr and a temperature of 770-790 K, a P-(1x1) phase is formed with H\textsubscript{2} desorption postulated, leading to a saturation surface coverage of 1 P/Si [14]. Further phosphine exposure (P \sim 10^{-7} Torr) at temperatures of 800<T<900 K leads to a P-(6\sqrt{3}x6\sqrt{3}) phase with a reported coverage of 3 P/Si [14]. At temperatures above 955 K the P-(1x1) phase returns, followed by a P-(2\sqrt{3}x\sqrt{3}) phase with island formation (970-1020 K), followed by another P-(1x1) phase (1020-1070 K), and finally returning to a clean Si(111)-(7x7) crystal at temperatures above 1070 K.

In this work we show that phosphine adsorbs onto Si(111)-(7x7) with an initial sticking coefficient of S\textsubscript{0}=1.0 at 120 K. Upon heating the adsorbed phosphine, hydrogen is removed from PH\textsubscript{x}(a) (3\geq x\geq 1) species to form Si-H bonds (T<700 K). Surface hydrogen then recombines to form H\textsubscript{2}(g) (T>700 K), followed by surface phosphorus recombination to form P\textsubscript{2}(g) (T>900 K). These results are qualitatively similar to those reported for PH\textsubscript{3} on Si(100) by Yu and Meyerson [12,13]. In addition, we show that: (1) Adsorbed PH\textsubscript{3} has two thermally activated reaction pathways which are coverage dependent. In the first pathway, molecularly chemisorbed PH\textsubscript{3} desorbs as PH\textsubscript{3}(g). In the second pathway, the reactive species PH\textsubscript{x} (3\geq x\geq 1) thermally decompose into H(a) and P(a); (2) A direct observation of P(a) recombination to produce P\textsubscript{2}(g) has been made. (3) P penetration into the near surface region occurs at 875 K.

In a separate paper we report additional studies of PH\textsubscript{3} adsorbed on Si(111)-(7x7), primarily employing electron stimulated desorption (ESD) methods [15].

II. Experimental

The experiments were carried out in a stainless steel ultra-high vacuum...
chamber with a base pressure of $\sim 3 \times 10^{-11}$ Torr, shown schematically in Fig. 1. The UHV system is equipped with a Varian Scanning Auger electron spectrometer (AES), a low energy electron diffraction (LEED)/electron stimulated desorption ion angular distribution (ESDIAD) apparatus, a collimated gas doser [16], and two digitally multiplexed UTI-100C quadrupole mass spectrometers (QMS). Further details of the UHV system have been given elsewhere [15,17].

One of the quadrupole mass spectrometers is shielded from the random gas flux arriving at the ionization source. This shielded QMS (SQMS) has two apertures. The first aperture is a small circular aperture (diameter = 5.0 mm) which is on the quadrupole axis. The aperture is electrically isolated from the shield, and has an applied potential of -100 V to prevent irradiation of the silicon crystal by electron emission from the ionization source when the crystal is on the quadrupole axis (i.e. during thermal desorption studies). The second and larger aperture is rectangular (5.32 cm x 3.42 cm) and lies directly above the ionization cage. This aperture may be opened or closed in vacuum by a retractable door driven by a rack and pinion. When the door to the larger aperture is open, the SQMS primarily probes the random gas flux, which may be used to detect the rate of adsorption of a gas when the crystal is in front of the gas doser [18]. When closed, the SQMS primarily probes those gases which are traveling along the quadrupole axis and serves as a detector of thermal desorption from the center of the Si crystal when it is located in front of the aperture. Normally the crystal is located $\sim 2$ mm in front of the aperture. The SQMS is pumped by three circular holes (diameter = 1.1 cm) equally spaced on the lower rear circumference of the shield. More details on the SQMS are given in [15].

The phosphine studies were performed on a 1.30 x 1.31 x 0.15 cm Si(111) p-type, B-doped 10 ohm-cm single crystal, oriented to within 1° of the
(111) direction. The crystal was chemically cleaned [19], mounted [16], and finally rinsed with methanol prior to installation into the vacuum chamber. For final cleaning in ultra high vacuum the crystal was sputtered with 2keV Ar\(^+\) at a crystal current of 2\(\mu\)A arriving at an incident angle of 70° with respect to the surface normal. After sputtering the crystal was subsequently annealed to 1175 K for 300-600 s, and slowly cooled to \(\sim\)120 K (rate <5 K s\(^{-1}\)). This cleaning procedure produced a well-ordered Si(111)-(7x7) surface, as determined by LEED, free of surface impurities detectable by AES.

To calibrate the flux of PH\(_3\) exiting the doser, the pressure drop in the gas handling system behind a nominal 2-micron conductance-limiting orifice was monitored over a period of 1.4x10\(^5\) sec. A plot of \(\ln[P(t)/P(0)]\) versus time, Fig. 2, gives a straight line with the slope, \(-F/V\), equal to the leak rate of phosphine from the gas handling system through the orifice and into the UHV chamber, where \(F\) is the conductance of the orifice in molecules-cm\(^3\) sec\(^{-1}\) and \(V\) is the volume behind the orifice (\(V=209.2\) cm\(^3\)). From the slope in Fig. 2 we obtain a conductance of 5.94x10\(^{-4}\) cm\(^3\) sec\(^{-1}\), to give a flux exiting the doser of \(F_{\text{phosphine}}=1.93\pm0.09\times10^{13}\) PH\(_3\)-molecules Torr\(^{-1}\) sec\(^{-1}\). The error reported for the flux is from a propagation of errors analysis.

The angular distribution of the phosphine effusing from the collimated doser is such that a portion of the flux misses the crystal. Campbell and Valone [20] and more recently Winkler and Yates [21] have shown that the flux intercepted by the crystal from a multicapillary-array collimator (diameter = 1.02 cm) can be determined from the known crystal-doser geometry. Using the method of Campbell and Valone [20] and a doser-crystal distance of 0.5 cm, we calculate that the fraction of the flux intercepted by a circular crystal of an area equal to our square crystal (d=1.474 cm) is \(f_{\text{ca}}=0.70\). The fraction of the flux intercepted by the crystal can also be obtained experimentally [18].
Figure 3 shows an adsorption kinetics experiment for phosphine on Si(111)-(7x7) at 121 K, as monitored by measurements of the PH$_3$ signal using the SQMS with the large aperture door open (i.e. probing the random PH$_3$ flux resulting from the PH$_3$ flux which is not adsorbed by the crystal). In this experiment, the doser is turned on at 113 s with the crystal rotated away from the beam. Upon achievement of a stable PH$_3$ signal at 316 s, the clean Si(111) crystal is rotated into the PH$_3$ beam and an immediate drop in the scattered PH$_3$ signal is observed as adsorption of PH$_3$ occurs. The adsorption occurs at a constant rate until 415 s, when the rate of adsorption suddenly decreases and the scattered PH$_3$ flux rises slowly to a limiting value. We assume that the initial constant sticking coefficient for PH$_3$ is unity. With this assumption [18], the fractional interception of the PH$_3$ flux by the crystal, $f_{\text{exp}}$, may be measured as $\Delta_1/(\Delta_1+\Delta_2)$. From Fig. 3 we measure $f_{\text{exp}}=0.65$. From 14 separate experiments we obtain a mean fractional interception of $f_{\text{exp}}=0.64 \pm 0.07$ (1σ) in good agreement with the calculated result ($f_{\text{calc}}=0.70$) based on the geometry of the system, as described previously. Thus, the assumption of an initial sticking coefficient, $S_0=1$, is physically reasonable based on the agreement between the experimental measurements of the fraction intercepted and the predicted value ($f_{\text{exp}}=f_{\text{calc}}$). The constancy of the initial sticking coefficient over a large coverage range also supports its value of unity.

For temperature programmed desorption (TPD) studies, a modified digital temperature programmer [22] was used to heat the crystal at a reproducible rate of $\sim 1.6$ K sec$^{-1}$ over the temperature range of 110 K to 1150 K. The SQMS was used in all the reported thermal desorption studies with the crystal reproducibly positioned $\sim 2$ mm in front of the smaller aperture and with the larger aperture closed. Both mass spectrometers were carefully calibrated for higher masses by leaking Kr into the UHV chamber.
The AES data reported herein represents the average of four measurements of the \( \text{d}N(E)/\text{d}E \) peak-to-peak heights taken at four points over the exposed area of the crystal. For Auger analysis, the electron gun typically delivered \( 2 \times 10^{-6} \) A in a 0.2 mm diameter beam at the crystal. An extensive study of the \( \text{P}^{(LVV)} \) lineshape and peak-to-peak amplitude showed no changes with prolonged electron beam exposure (up to 7.5 times the analysis time); therefore, the reported AES accurately measures the relative phosphorus surface coverage originating from strongly-bound \( \text{PH}_x \) \((3 \leq x \leq 1)\) species which have been decomposed in the electron beam; the phosphorus surface coverage measurement should be considered as an assay of the strongly-bound \( \text{PH}_x \) species which are not desorbed by ESD. The reported phosphorus concentrations were calculated from the AES measurements using the appropriate elemental sensitivity factors [23].

III. Results

A. Adsorption of \( \text{PH}_3/\text{Si}(111) \).

The kinetics of adsorption of phosphine on \( \text{Si}(111)-(7\times7) \) at 121 K can be observed as shown in Fig. 3. Once the crystal is rotated into the \( \text{PH}_3 \) flux, \( \text{PH}_3 \) adsorbs at a constant rate up to \(-1.6 \times 10^{14}\) \( \text{PH}_3 \)-molecules cm\(^{-2}\) (plateau region of constant rate of uptake). Eleven separate adsorption experiments gave a mean exposure value for the constant uptake region to be \( 1.5 \pm 0.2 \times 10^{14} \) \( \text{PH}_3 \)-molecules cm\(^{-2}\). After the region of constant uptake, the \( \text{PH}_3 \) adsorption process becomes less efficient, indicating a decreasing sticking coefficient. The adsorption temperature throughout these adsorption experiments was \( T_{\text{ads}} = 116 \pm 5 \) K.

Phosphine adsorption on \( \text{Si}(111)-(7\times7) \) is further confirmed by the AES detection of surface phosphorus after the crystal is exposed to \( \text{PH}_3 \) (Fig. 4). On the basis of the Auger data in Fig. 4 where the increase of the phosphorus...
coverage is measured versus PH₃ exposure, we estimate that about 70-75% of the PH₃ species detected by Auger spectroscopy adsorbs during the process with S=1, and 25-30% during the process with S<1.

B. Desorption from PH₃/Si(111)

All the desorbing species observed from temperature programmed desorption of PH₃, adsorbed to saturation coverage on Si(111)-(7x7) at 120 K, are shown in Fig. 5. The thermal desorption data reveal two reaction pathways for adsorbed PH₃. In the first pathway, molecularly adsorbed PH₃ desorbs intact from the surface. In the second pathway, chemisorbed PHₓ(a) (3≥x≥1) thermally decomposes to H(a) and P(a) species, which subsequently desorb as H₂(g) and P₂(g).

A thorough search for other desorbing species showed no other reaction products. Other products of primary concern were SiH₄ (m/e=32 and its fragment 30 (SiH₂⁺)); Si₂H₆ fragment Si₂H₅⁺ (m/e=61); SiP (m/e=59); P₂H₄ (m/e=66); and P₄ (m/e=124). In the case of SiH₃⁺ and Si₂H₆⁺ an interference occurs with P⁺ and P₂⁺ respectively; however, SiH₄ and Si₂H₆ may be eliminated as possible desorption products due to the lack of signal for their other known ionization fragments at 30 amu (SiH₂⁺), 29 amu (SiH⁺), 60 amu (Si₂H₄⁺), and 58 amu (Si₂H₂⁺) which do not coincide with the observed desorption species. No evidence for the desorption of any of these possible silane and disilane product species was found in these experiments.

The desorption of the molecular PH₃ does not occur if the PH₃ coverage is less than 1.5x10¹⁴ PH₃ cm⁻². This means that in the exposure region where S=1 (Fig. 3), all of the adsorbed PH₃ will dissociate upon heating.

The desorption of the molecularly-bound PH₃ state as a function of PH₃ exposure is shown in Figs. 6 and 7. The molecular desorption of PH₃ exhibits a
desorption peak maximum at ∼180 K with additional desorption processes extending to ∼550 K. The large temperature range for PH₃ desorption in Fig. 6 suggests that several PH₃ chemisorption states are responsible for the molecular desorption of P₃. From Fig. 7 one can clearly see that the molecularly adsorbed PH₃ state, measured by thermal desorption, does not saturate until PH₃ exposures greater than ∼35x10¹⁴ PH₃ cm⁻² have occurred; however the data in Fig. 4 shows that the phosphorus surface concentration as measured by Auger spectroscopy saturates at an exposure of ∼5x10¹⁴ PH₃ cm⁻². The lack of increase in the P Auger intensity beyond a PH₃ exposure of ∼5x10¹⁴ PH₃ cm⁻² suggests that the coverage of molecular PH₃ responsible for PH₃ desorption is small. This idea is verified in Fig. 5 by comparing the integrated thermal desorption yield of PH₃(g) to that of H₂(g). Note that mass spectrometer sensitivity for H₂(g) is 10⁻² compared to that for PH₃(g). The small relative yield of PH₃ compared to H₂ (coming from dissociation of PH₃) suggests that only a small coverage of PH₃ which desorbs as molecular PH₃ is present even after an exposure of ∼35x10¹⁴ PH₃ cm⁻².

Figure 8 shows the thermal desorption behavior of P₂ from Si(111) exposed to PH₃. The desorption of phosphorus exclusively as P₂(g) is expected at the low pressures of the TPD experiments, where considerations of equilibrium would strongly favor P₂ production. This was confirmed experimentally where both P₄⁺ (m/e=124 amu) and P₃⁺ (m/e=93 amu) were shown to be absent (see ref. 25 and 26 for P₄ cracking pattern information).

The ionization cracking pattern of P₂(g) has been obtained by heating InP or GaP to temperatures above 870 K [27,28]. The ionization of P₂(g) with 70 eV electrons is reported to give a fragmentation pattern of P₂⁺:P⁺ in the ratio of 100:12, respectively [28]. From the inset in Fig. 8, the ratio of the desorption yields of P₂⁺ and P⁺ from Si(111) is approximately 100:67. Despite
the difference in cracking patterns between the literature [28] and the work reported here, the agreement in the desorption peak shapes for \( P_2 \) and \( P \) strongly suggests that the two species are related, and that \( P^+ \) is a mass-spectrometer cracking product of \( P_2 \). The symmetric shape of the \( P_2 \) desorption features (Fig. 8), and the \( T_{\text{max}} \) shift towards lower temperatures with increasing initial coverage, suggest that \( P_2 \) desorbs with second order kinetics. Using second order kinetics, the activation energy of desorption for \( P_2 \) from \( P/\text{Si}(111) \) at the zero coverage limit was estimated to be \( E_d = 87 \text{ kcal mole}^{-1} \), using the method of Chan, Aris and Weinberg [29] and the second-order pre-exponential factor at the zero coverage limit was estimated to be \( v_d = 10^{2 \pm 1} \text{ cm}^2 \text{ sec}^{-1} \). To calculate the pre-exponential factor we assumed that all 19 dangling bonds in the \( \text{Si}(111)-(7x7) \) cell [30] are reactive and there is 1P/\( \text{Si} \)-dangling bond on a fully-covered surface. Arguments to be presented later suggest that a P coverage of 1P/\( \text{Si} \)-dangling bond is possible sterically when \( \text{PH}_3 \) is the adsorbate. However, this assumption may not be strictly accurate, considering that different reactivity of the \( \text{Si}(111)-(7x7) \) dangling bonds may exist, as has been observed for \( \text{NH}_3 \) on \( \text{Si}(111) \) [31].

A major desorption product shown in Fig. 5 is molecular hydrogen. This desorption process corresponds closely to that observed when atomic H is adsorbed on \( \text{Si}(111) \) in the monohydride adsorption state [32], as will be shown below.

C. \( \text{Si}(111) \) Site Blocking by Deuterium.

It is well-known that the pre-adsorption of atomic deuterium (or hydrogen) onto silicon will cap the surface dangling bonds and reduce the adsorptive capacity of the surface. This effect has been observed for the \( \text{NH}_3/D/\text{Si}(100) \) system [17] and for the adsorption of unsaturated hydrocarbons on \( \text{Si}(100) \) [33].
Similar results are observed for the PH3/D/Si(111)-(7x7) system, demonstrating that the dangling bonds are the active sites for phosphine adsorption.

The atomic deuterium is produced by the dissociation of D2(g) on a tungsten filament at 1800 K [17]. The atomic D exposures are reported in Langmuirs (L) of D2(g) exposed to the W-filament, where 1 L=1x10^-6 Torr-sec (uncorrected for ion gauge sensitivity to D2). The well-known β1-monodeuteride and β2-dideuteride desorption states develop on Si(111) with increasing exposure to atomic D, as shown in Fig. 9. To calibrate the D(a) coverage, the onset of the surface dideuteride production (5 L D2), as observed by the desorption of the well-known β2-D2 state, was taken as an index of monolayer D(a) coverage, as shown in the inset of Fig. 9. This is an arbitrary criterion of the monolayer capacity for D, and it is observed from the data in Fig. 9 that the β1 (monodeuteride) desorption yield continues to increase above this arbitrarily-defined monolayer point.

The effect of pre-adsorbed deuterium on the PH3 adsorption kinetics is to decrease the amount of adsorbed PHx. The decrease in the amount of PHx adsorbed, with increasing D(a) coverage, is indicated by the drop in the surface phosphorus concentration as measured by AES (Fig. 10) for a saturation PH3 exposure on the D-capped Si(111) surface. The surface is passivated by a 7-L D2 exposure which is near the onset of the β2-dideuteride production, as shown in Fig. 9 for the D atom experiments.

A search for deuterium-labelled phosphine desorption products, shown in Fig. 11, clearly indicate that no isotope exchange processes occur on the Si(111) surface between molecularly adsorbed PH3 and D(a). This result indicates that recombination of a PHx(a) species with H(a) is not responsible for either the sharp PH3 desorption feature (T~180 K) or for the PH3 desorption processes up to ~550 K (as seen in Figs. 5 and 6).
For atomic D coverages yielding the \( \beta_2 \) (dideuteride) desorption state, etching of the Si surface was observed as indicated by the desorption product \( \text{SiD}_4 \). This result agrees with the observed etching of silicon surfaces by hydrogen recently reported by Greenlief et al. [34].

D. Phosphine Adsorption on P/Si(111).

A saturated, phosphine-covered Si(111) surface may adsorb additional \( \text{PH}_3 \) if the pre-adsorbed \( \text{PH}_3 \) is heated sufficiently to remove the adsorbed hydrogen. In Fig. 12 the P(LVV) AES peak-to-peak intensity is reported for experiments involving \( \text{PH}_3 \) exposure followed by heating to two different temperatures, followed by a re-exposure to \( \text{PH}_3 \) at 115 K. In the first thermal treatment, the saturated \( \text{PH}_3 \) layer (exposure = \( \epsilon_1 \)) was heated to below the onset of the \( \text{H}_2 \) desorption (615 K), as indicated by the dashed arrow in Fig. 12, and re-exposed to another saturation exposure of \( \text{PH}_3 \), \( \epsilon_2 \). A slight increase in the P(LVV) peak-to-peak intensity after the second exposure indicates that only a very small additional adsorption of \( \text{PH}_3 \) can take place on the \( \text{PH}_3 \) pre-covered surface which still contains adsorbed hydrogen produced by \( \text{PH}_3 \) thermal decomposition.

In the second experiment the surface containing the saturated \( \text{PH}_3 \) exposure, as produced by \( \epsilon_1 \), was heated to 875 K, which is beyond the \( \text{H}_2 \) desorption temperature but prior to the \( \text{P}_2 \) desorption temperature. The crystal was then re-exposed to a second saturation exposure of \( \text{PH}_3 \), \( \epsilon_2 \). In the second exposure, the kinetic uptake curve was identical to that shown in Fig. 3 (not shown), and the P(LVV) peak-to-peak intensity doubles over that of the first exposure (Fig. 12). This behavior indicates a regeneration of \( \text{PH}_3 \) adsorption sites on the Si(111) surface upon desorption of hydrogen.

The Si(111) surface has a large capacity for the adsorption of phosphorus. The exposure-anneal-exposure cycle, described above, can be repeated several
times without a significant attenuation in the Si(111) adsorption capacity for PH₃, as shown by the increase of the P(LVV) AES peak-to-peak intensity with incremental PH₃ exposures in Fig. 13. A change in the surface structure between the clean Si(111)-(7x7) structure and the P/Si(111)-(1x1) structure after e₅ was also observed by LEED (not shown), in agreement with the work of van Bommel et al. [11].

A small increase in the P(LVV) peak-to-peak intensity also occurs when the PH₃-covered surface is heated to cause removal of surface hydrogen. This small, although reproducible, increase in P(LVV) peak-to-peak intensity is due to the thermal loss of P-H bonds that slightly affects the P(LVV) lineshape and slightly increases the measured peak-to-peak intensity. Further details of the effects of hydrogen on the P(LVV) and Si(LVV) AES signals are given in another paper [15].

Studies of the behavior of the Si(LVV) Auger intensity were also carried out during the PH₃ exposure-anneal-exposure cycles. The increase in the atomic fraction of P upon sequential adsorption-anneal cycles is accompanied by a concomitant decrease in the Si(LVV) AES intensity as shown in Fig. 14.

IV. Discussion.

A. Saturation Coverage PH₃/Si(111) at 120 K.

The adsorption of PH₃ on Si(111)-(7x7) occurs at 120 K at a constant rate corresponding to unit adsorption efficiency up to 1.5±0.2x10¹⁴ PH₃-molecules cm⁻². If we assume that PH₃ adsorbed during the S=1 process is the primary source of reactive PHₓ, which ultimately forms surface phosphorus, then an estimate of the PHₓ saturation coverage can be made. From the measured PHₓ coverage at the end of the S=1 process and the additional phosphorus uptake,
measured by AES, during the Si(111) process (see Fig. 4), the PH\textsubscript{X} species saturation coverage, produced from PH\textsubscript{3}, is calculated to be 1.9±0.3x10\textsuperscript{14} PH\textsubscript{X} cm\textsuperscript{-2} at 120 K.

From STM measurements the ideal Si(111)-(7x7) surface has 19 dangling bonds, (d-b), or reactive sites per unit cell [31], which corresponds to 3.0x10\textsuperscript{14} Si d-b cm\textsuperscript{-2}. Therefore, the PH\textsubscript{X} species saturation coverage can also be expressed as $\theta_{\text{sat}}$=0.5-0.7 PH\textsubscript{X}/Si-dangling bond.

The assumption of equal participation of all 19 dangling bonds in the unit cell may not be accurate. Different reactivity of the Si(111)-(7x7) dangling bonds has been observed for NH\textsubscript{3} on Si(111) [31]. For ammonia on Si(111)-(7x7) the rest-atoms were found to be most reactive (6 d-b) followed by the adatoms (12 d-b). The center-adatoms in the (7x7) unit cell also were found to be more reactive to NH\textsubscript{3} than corner-adatoms in a ratio of reactivity of ~2:1. The reactivity towards NH\textsubscript{3} was not reported for the Si-dangling bonds in the holes at the corners of the (7x7) cell; therefore, we assume that the Si-dangling bonds in the holes at the corners of the (7x7) cell are non-reactive. If PH\textsubscript{3} adsorbs on Si(111) as NH\textsubscript{3} does, then there would be 15 dangling bonds per unit cell (6 rest-atoms + 6 center-adatoms + 3 corner-adatoms = 15 d-b/unit cell). For this type of bonding scheme the PH\textsubscript{X} saturation coverage would be ~0.7-0.9 PH\textsubscript{X}/Si-dangling bond.

B. Adsorption Kinetics - PH\textsubscript{3}/Si(111)

The kinetics of adsorption of PH\textsubscript{3} on Si(111)-(7x7) at 120 K show clearly that the initial sticking coefficient is unity, and that it remains constant for a coverage extending up to ~75% of the saturation coverage for chemisorbed PH\textsubscript{X} species. The large range of coverages which exhibits constant sticking coefficient kinetics clearly indicates that adsorption occurs via an extrinsic mobile precursor state, and that the lifetime of the precursor is long enough for
migration to occur over filled states to empty adsorption sites.

The end of the S=1 adsorption process in Fig. 3 is marked by an abrupt transition between S=1 and S<1. It is worthwhile to speculate as to the nature of this transition. One possibility is that adsorbed PHX sterically blocks incoming PH₃ molecules, decreasing the adsorption probability (S<1). A test of such a model is to "pack" PH₃ into the Si(111)-(7x7) cell (6.27x10⁻¹⁴ cm²) using the van der Waals radii for PH₃ (r=1.72 Å [35]). A cubic packing of PH₃ would produce ~53 PH₃/Si-unit cell and close-packing (hcp) would produce ~61 PH₃/Si-unit cell. Both of these packing arrangements sterically allow considerably more than 1 PH₃/dangling bond. Therefore, we must conclude that steric blocking arguments cannot account for the abrupt change in the kinetics of the adsorption process. Another possibility is that PH₃ adsorbs predominantly dissociatively as PHX (2≥x≥1) in the S=1 region [13,15]. The PH₃ coverage at the end of the constant uptake region (S=1) is 9 PH₃/Si-unit cell (1.6x10¹⁴ PH₃ cm⁻²) consistent with a model where PH₃ may adsorb dissociatively in the S=1 region primarily as PH₂(a) and H(a), with PH₂(a) and H(a) together occupying 15-19 dangling bond sites. If PH₃ dissociatively adsorbs initially as PH₂(a) + H(a), then both PH₃ and NH₃ adsorb on Si(111)-(7x7) in the same manner [31,36].

C. Adsorption Kinetics for PH₃/D/Si(111).

Blocking the Si(111) dangling bond sites by pre-adsorbed D atoms prevents PH₃ adsorption. This is observed by a reduction in the surface phosphorus concentration achieved by PH₃ adsorption on Si(111) containing increasing deuterium coverages. These results indicate that the Si-dangling bonds are the adsorption sites for PH₃ on Si(111)-(7x7). To within the accuracy of our measurements, it may be concluded that a saturated monodeuteride coverage is
sufficient to block PH$_3$ adsorption on Si(111)-(7x7).

D. Thermal Desorption from PH$_3$/Si(111)

The thermal desorption results indicate that adsorbed phosphine has two reaction pathways. In the first pathway, molecularly adsorbed PH$_3$ desorbs as PH$_3$(g), with no observable surface chemistry. In the second pathway, adsorbed PH$_x$ decomposes into P(a) and H(a), which eventually desorbs as H$_2$(g) (T$>$700 K) and P$_2$(g) (T$>$900 K). The desorption of P$_2$(g) has been reported from PH$_3$ decomposition on Si(100) [13]. Further details of the thermal decomposition of PH$_x$ adsorbed on Si(111)-(7x7) are given elsewhere [15].

E. Phosphine adsorption on P/Si(111)

If an adsorbed layer of PH$_3$ is heated beyond the hydrogen desorption temperature and below the phosphorus desorption temperature (T$<$875 K), then additional PH$_3$ may be adsorbed onto the P/Si(111) layer. This process may be repeated several times before saturation occurs, showing the large capacity of Si(111) for adsorption of phosphorus.

As the P(LVV) peak-to-peak intensity increases with the incremental PH$_3$ exposures (Fig. 13), the Si(LVV) peak-to-peak intensity decreases, as shown in Fig. 14. The attenuation of the Si(LVV) peak-to-peak intensity is caused by P screening of Si atoms. A simple estimate of the thickness of the adsorbed phosphorus after $c_5$ may be obtained from the observed attenuation of the Si(LVV) AES intensity by using the expression $d = \lambda \ln(I_0/I)$, where $d$ is the thickness of the phosphorus layer, $\lambda$ is the escape depth of the Si(LVV) Auger electron through a phosphorus layer ($\lambda \approx 5\AA$ [37]), and $I_0$ is the initial Si(LVV) intensity. Based on this expression, the calculated value of $d = 1\ \AA$. This is equivalent to a P coverage of 3.6-5.2x10$^{14}$ P cm$^{-2}$ depending on the density
(g cm\(^{-3}\)) assumed for overlayers of P.

The distribution in depth of the surface phosphorus may be inferred from
the P coverage causing the observed screening of the Si AES signal. We assume
from our quantitative uptake measurements that the PH\(_x\) coverage (following
\(\epsilon_1\)) = 1.9±0.3x10\(^{14}\) PH\(_x\) cm\(^{-2}\) corresponding to a P(LVV) AES intensity of 1.6
arbitrary units (no heating, Fig. 12). After 5 cycles of PH\(_3\) adsorption to \(\epsilon_5\),
the P(LVV) AES intensity has increased to 7.8 arbitrary units. If all of this P
was on the surface, the coverage would be 9.3±1.5x10\(^{14}\) P cm\(^{-2}\). If penetration of
some of the P has occurred as a result of the successive annealing cycles, the
number of P atoms cm\(^{-2}\) would exceed 9.3±1.5x10\(^{14}\) P cm\(^{-2}\). Thus, the attenuation of
the Si(LVV) Auger intensity by P corresponds to a considerably lower surface
coverage of P (3.6-5.2x10\(^{14}\) P cm\(^{-2}\)) than is measured from the P(LVV) intensity
calibrated against a quantitative PH\(_3\) uptake measurement. This implies that
substantial P penetration into the near surface region of Si(111) has occurred
upon annealing to 875 K. This subsurface P can be liberated as P\(_2\)(g) on heating
as shown in Fig. 8.

V. Summary

The behavior of phosphine on Si(111)-(7x7) studied by AES and TPD may be
summarized as follows:

1. Phosphine adsorbs onto Si(111)-(7x7) at 120 K into a reactive PH\(_x\)
   \((3\geq x \geq 1)\) species with a sticking coefficient of \(S=1\) up to ~75% of the
   PH\(_x\) saturation coverage.

2. The saturation coverage of reactive phosphine species on Si(111) is
   approximately 0.5-0.7 PH\(_x\)/Si-dangling bond (assuming 19 dangling bonds
   per Si(111)-(7x7) unit cell).
3. At coverages greater than ~1.5x10^{14} \text{ PH}_3 \text{ cm}^{-2}, a molecularly-bound \text{ PH}_3 state exists which does not lead to any thermally-induced surface chemistry. This \text{ PH}_3(a) species is present at a coverage corresponding to a small fraction of a monolayer.

4. Surface Si-H species formed by \text{ PH}_X thermal decomposition recombine to desorb as H_2(g) at T \geq 700 \text{ K}, and surface Si-P bonds break to yield P_2(g) at T \geq 900 \text{ K}. The kinetic parameters for second order desorption of P_2(g) are v_d = 10^{2\pm1} \text{ cm}^2 \text{ sec}^{-1} and E_d = 87 \text{ kcal mole}^{-1}.

5. Phosphine may be used as a source for the continued deposition of surface phosphorus, after removal of surface hydrogen. Phosphorus penetration into the bulk occurs to some degree following heating to 875 K.

6. Acknowledgements

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References

37. C.J. Powell, private communication. Here it is assumed that $\lambda_p = \lambda_{S1} = 5 \, \text{Å}$ at 92 eV.
Figure Captions

Figure 1. Schematic of the UHV chamber used in these studies.

Figure 2. Calibration of the PH₃ flux from the doser.

Figure 3. Adsorption kinetics for PH₃ on Si(111)-(7x7) at 121 K. Flux of PH₃ at the crystal = $1.6 \times 10^{12}$ PH₃ molecules cm$^{-2}$ sec$^{-1}$. $P_0$(PH₃) = 0.214 Torr. The PH₃ pressure "spike" at t=1512 s is due to mechanical shock to the cooling coils which have adsorbed PH₃ from the background gas.

Figure 4. The surface concentration of phosphorus with increasing PH₃ exposure as probed by AES. Error bars represent 1σ deviation from the average of 4 AES measurements taken over the crystal area. The ordinate represents the atomic fraction of P in the depth of Auger sampling.

Figure 5. Thermal desorption spectra of all the desorbing species observed from PH₃/Si(111)-(7x7). The temperature ramp used in these studies was $dT/dt = 1.6$ K sec$^{-1}$. Comparison of the integrated area of the PH₃ to that of H₂ suggest that the observed PH₃(g) corresponds only to a small fraction of a monolayer.

Figure 6. Thermal desorption of molecular PH₃ from the molecularly-bound PH₃ surface state on Si(111).

Figure 7. Integrated TPD yield of molecular PH₃ as a function of surface exposure to PH₃ for the TPD curves shown in Fig. 6. Note: saturation occurs at PH₃ exposures greater than $\sim 35 \times 10^{14}$ PH₃ cm$^{-2}$.
Figure 8. Thermal desorption yield of P$_2$ as a function of PH$_3$ exposure. Inset shows the P$_2^+$ and P$^+$ mass spectrometer traces. The PH$_3$ exposures (x10$^{14}$ PH$_3$ cm$^{-2}$) are a: 0.7, b: 1.4, and c: 6.9 (saturated). The linear heating rate through the P$_2$ desorption features was dT/dt= 1.5 K s$^{-1}$.

Figure 9. Deuterium coverage calibration for phosphine-deuterium co-adsorption studies. D$_2$ exposures are reported in Langmuirs of D$_2$. The onset of the dihydride production as observed by TPD is arbitrarily defined as 1 monolayer D coverage (~5L D$_2$ in this case).

Figure 10. The effect capping the Si-dangling bonds, with atomic deuterium, on the adsorption of PH$_3$ measured by Auger spectroscopy. PH$_3$ exposure= 2.7x10$^{14}$ PH$_3$ cm$^{-2}$ at 130 K.

Figure 11. Thermal desorption from PH$_3$ co-adsorbed on a partially capped D/Si(111)-(7x7) surface. No isotope mixing to produce deuterated phosphine species is observed. D$_2$ exposure= 3 L; PH$_3$ exposure= 3.0x10$^{14}$ cm$^{-2}$.

Figure 12. The re-adsorption capacity of an exposed PH$_3$/Si(111) surface after annealing to 615 K or to 875 K. Incremental exposures are 17.4x10$^{14}$ PH$_3$ cm$^{-2}$, a saturation exposure.

Figure 13. The addition of surface phosphorus by repetitive exposure-anneal-exposure cycles of PH$_3$ on Si(111) as probed by the P(LVV) AES signal. The adsorption temperature was 115 K and the subsequent annealing temperature was 875 K. P$_2$ does not desorb at 875 K.
Figure 14. The attenuation of the Si(LVV) AES signal during the exposure-anneal-exposure cycles of PH₃ on Si(111). Adsorption temperature was 115 K and annealing temperature was 875 K. See Fig. 13.
Ultrahigh Vacuum Apparatus for Silicon Surface Chemistry

Taylor, Wallace, Choyke, Yat
Figure 1
Doser Calibration for PH$_3$

\[ \text{Slope} = \frac{F}{V} = -2.838 \times 10^{-6} \text{ sec}^{-1} \]

\[ \left[ \frac{dn}{dt} \right]_{PH_3, P_0} = 6.62 \times 10^{12} \text{ PH}_3/\text{sec} \]

\[ \ln \left( \frac{P(t)}{P(0)} \right) \]

\[ P_0 = 0.343 \text{ Torr} \]

Temp=296.7 K

Gas line Volume=209.2 cm$^3$

Time (10$^4$ seconds)
Adsorption of Phosphine on Si(111)–(7x7)

$P_0 = 0.214 \text{Torr}$

$T_{\text{ads}} = 121 \text{ K}$

QMS Signal ($m/e = 34$)

$S_0 = 1.0$

$\epsilon_{\text{PH}_3} = 1.6 \times 10^{14} \text{ PH}_3/\text{cm}^2$

Time (s)
AES Measurements of Phosphorus Surface Concentration

with increasing PH$_3$ exposure. Si(111)-(7x7)

$T_{ads} = 120$ K

P Concentration (atomic fraction)

Limit of Detection

PH$_3$ Exposure ($\times 10^{14}$ molecule cm$^{-2}$)
Thermal Desorption from PH$_3$/Si(111)-(7x7)

$\varepsilon_{PH_3} = 18.6 \times 10^{14}$ PH$_3$/cm$^2$

$\frac{dT}{dt} = 1.6$ K/s

- H$_2 \times 10^{-2}$
- PH$_3$ x1
- P$_2$ x1

QMS Signal

Temperature (K)

100 300 500 700 900 1100 1300

10$^{-9}$ A

2 amu

34 amu

62 amu
Thermal Desorption of Molecularly Bound PH$_3$. Si(111)-(7x7)

\[ T_{ads} = 120 \text{ K} \quad \text{d}T/\text{d}t = 1.6 \text{ K/s} \]

QMS Signal (m/e=34)

\[ 10^{-9} \text{ Amps} \]

PH$_3$ Exposure

\[ \times 10^{14} \text{ PH}_3/\text{cm}^2 \]

Temperature (K)

100 300 500 700 900 1100 1300

- 72.5
- 38.5
- 9.5
- 4.8
- 1.5
Thermal Desorption Yield of PH$_3$ from PH$_3$ Adsorption on Si(111) at 120 K

![Graph showing the relationship between PH$_3$ TPD yield and PH$_3$ exposure.](image)
Thermal Desorption of $P_2$ from PH$_3$. Si(111)–(7×7)
Thermal Desorption of D$_2$ from D/Si(111)

![Graph showing the thermal desorption of D$_2$ from D/Si(111). The graph displays the relationship between QMS signal (m/e = 4) and temperature (K). The inset shows the mass spectrum with peaks labeled as Monohydride ($\beta_1$) and Dihydride ($\beta_2$). The main graph shows the exposure (Langmuirs, D$_2$) and temperature relationship with peaks labeled $\beta_1$ and $\beta_2$. The y-axis represents the $D_2^+$ yield (arb. units), and the x-axis represents the temperature (K). The graph includes a scale for exposure (L, D$_2$) and current (2x10$^{-7}$ Amps).]
Isotope Exchange Experiment for PH$_3$/D/Si(111)-(7x7)

\[ \frac{dT}{dt} = 1.6 \text{ K s}^{-1} \]

![Graph showing QMS signal vs. Temperature (K) with peaks for PH$_3^+$, PHD$^+$, PH$_2$D$^+$, PD$_2^+$, and PHD$_2^+$]
Additional PH₃ Uptake on Saturated PH₃/Si(111) after Annealing to Different Temperatures

\[ E_n = 17.4 \times 10^{14} \text{ PH}_3/\text{cm}^2 \]

\( T_{\text{dose}} = 115 \text{ K} \)

Heat to 875 K

Heat to 615 K

Incremental PH₃ Exposures

P(LV) AES Signal (arb. units)
Addition of Phosphorus to Si(111) by Thermal Decomposition of Adsorbed PH$_3$ and H$_2$ Removal

\[ \varepsilon_n = 1.74 \times 10^{14} \text{PH}_3 / \text{cm}^2 \]

\[ T_{\text{dose}} = 115 \text{ K} \]

\[ T_{\text{heat}} = 875 \text{ K} \]

P(LVV) AES Signal (arb. units)

Incremental PH$_3$ Exposures

$\varepsilon_1, \varepsilon_2, \varepsilon_3, \varepsilon_4, \varepsilon_5$
The Reduction of the Si(LVV) AES Intensity by the Incremental Addition of Phosphorus from Decomposition of PH₃ on Si(111)

\[ E_n = 17.4 \times 10^{14} \text{ PH}_3 / \text{cm}^2 \]

Incremental PH₃ Exposures

\( E_1 \)
\( E_2 \)
\( E_3 \)
\( E_4 \)
\( E_5 \)

Si(LVV) AES Signal (arb. units)
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