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In-situ production of PH$_3$ from red phosphorus and atomic hydrogen

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Abstract

The production of PH$_3$ from red phosphorus and the atomic hydrogen formed in the catalytic decomposition of H$_2$ on heated W surfaces was confirmed. The absolute density of the PH$_3$ could be as high as $10^{13}$ cm$^{-3}$; the density was proportional to H-atom density in the absence of red phosphorus, although three H atoms must be involved in the production of one PH$_3$ molecule, but showed minor dependence on the amount of red phosphorus. These results suggest that the rate-determining step for the production of PH$_3$ is that which produces H atoms.
1. Introduction

PH$_3$ is one of the most important dopant gases in semiconductor industries and has been used in many chemical vapor deposition processes [1-19]. The problem is that PH$_3$ is not only highly toxic but also explosive. Thus it is desirable to produce it in-situ rather than store it in high-pressure cylinders. Naitoh et al. have reported the in-situ production of PH$_3$ from phosphorus vapor, possibly P$_2$ and P$_4$, and hydrogen plasma [20,21]. They have succeeded in preparing high-quality InP films by this technique. In addition, they have suggested the production of PH$_3$ from H atoms and solid phosphorus deposited on chamber walls [21]. However, no quantitative analyses have been made for this PH$_3$ production process. The absolute density of PH$_3$ has not been evaluated, either.

In the present study, we tried to produce PH$_3$ in a reaction between solid red phosphorus and the atomic hydrogen formed in the catalytic decomposition of H$_2$. It is now well established that H atoms can be produced efficiently from H$_2$ on heated W catalysts [22]. The absolute densities of H atoms and PH$_3$ were measured to obtain information on the PH$_3$ production mechanism.

2. Experimental

The experimental procedure and apparatus were similar to those described elsewhere [23-26]. H atoms were produced by the catalytic decomposition of H$_2$ on a heated W wire installed in a chamber evacuated with a turbomolecular pump. The pressure and the flow rate of H$_2$ were kept constant at 40 Pa and 100 sccm (1 sccm = $6.9 \times 10^{-7}$ mol s$^{-1}$), respectively, and the H-atom density was varied by changing the wire temperature from 1630 to 2570 K. The wire length and diameter were 30 cm and 0.38 mm, respectively. The catalyst temperature was evaluated from its electric resistivity. One or two pellets of red phosphorus, 14 mm in
diameter and 1mm in thickness, were placed in a glass beaker in the vacuum chamber. The distance between the W wire and the phosphorus pellets was changed between 9 and 12 cm. The typical distance was 12 cm.

PH$_3$ produced in the reaction between H atoms and red phosphorus was detected mass spectrometrically. A quadrupole mass-spectrometer was attached to the chamber through a sampling hole (0.1 mm in diameter). The flight tube was differentially pumped with another turbomolecular pump. The absolute density was determined by flowing known amounts of PH$_3$, diluted with He and H$_2$, and measuring the mass signals. The total pressure in the chamber was also kept at 40 Pa in this calibration measurement.

H-atom density was measured with a two-photon laser-induced fluorescence technique following excitation at 205.1 nm [22]. The distance between the W wire and the laser beam was 9 cm. The absolute densities of H atoms were evaluated from Lyman-$\alpha$ absorption measurements at 121.6 nm [22].

H$_2$ (Japan Air Gases, 99.999%) and PH$_3$ (Japan Air Gases, diluted with He to 2.0%) were used from cylinders without further purification. The purity of the PH$_3$ was 99.9995%, while that of the He was 99.9999%. The red phosphorus was a product of Kanto Kagaku and the purity was 98.0%.

3. Results

Figure 1 shows typical mass spectra when the W wire was heated in the presence of H$_2$ and red phosphorus. This figure also includes a mass spectrum of PH$_3$, recorded without heating the W wire. The similarity in the mass patterns confirms the production of PH$_3$ from H atoms and red phosphorus. The peak intensity ratio corresponding to the mass numbers of 31, 32, 33, and 34 for PH$_3$ was 11:42:11:36, while that at 2570 K was 12:42:12:34. The ratios
were similar at 2340 and 1930 K. In the H₂ and red phosphorus system, PH₃ could only be detected when the wire temperature was higher than 1790 K, which corresponds to the H-atom density of 2×10¹² cm⁻³. The PH₃ density when the catalyst temperature was 2570 K was evaluated to be as high as 1.3×10¹³ cm⁻³. The number of phosphorus pellets had a minor effect on the PH₃ signal. Figure 2 illustrates the dependence of the densities of H atoms and PH₃ molecules on catalyst temperature. The H-atom density was measured in the absence of phosphorus pellets. The activation energy for the production of PH₃, evaluated from the slope of the plot in Fig. 2, depended little on the distance between the wire and the pellet, number of pellets, or the H₂ pressure. As is shown in this figure, the two plots are parallel and the apparent activation energies for the production of H atoms and PH₃ molecules, 228±6 and 215±7 kJ mol⁻¹, respectively, agree within the error limits. In other words, the PH₃ density is proportional to the H-atom density, although three H atoms must be involved in the production of one PH₃ molecule. The H-atom density in the absence of phosphorus pellets must be proportional to the production rate of H atoms. The activation energy for the production of H atoms agrees with results reported previously [22]. No signals for P₂ and P₄ could be observed even when the catalyst was heated. Such mass signals have not been observed by Naitoh et al. when the phosphorus sample was not heated, either [21].

The surface temperature of phosphorus pellets may increase when the W wire is heated. However, this increase should be minor. It has been shown that thermal radiation has little influence on substrate temperature when the distance between the catalyst and the substrate is more than 10 cm [27]. It should also be noted that there was no hysteresis in the PH₃ density when the catalyst temperature was increased or decreased. Former laser-induced fluorescence measurements also have revealed low gas temperatures several centimeters from the catalyst [23-25,28-30].
4. Discussion

The minor dependence of the PH$_3$ density on the amount of red phosphorus, as well as the proportionality between the PH$_3$ density and the production rate of H atoms, suggests that the rate-determining step for the production of PH$_3$ is that of H atoms. Similar proportionality between the H-atom density and the reaction rate has been observed in the photoresist removal processes [26]. The following sequential production mechanism of PH$_3$ may be assumed:

\[
\begin{align*}
H_2 & \rightarrow 2H \quad \text{on catalysts,} \\
P(\text{solid})+H & \rightarrow \text{PH(adi)}, \\
\text{PH(adi)}+H & \rightarrow \text{PH$_2$(adi)}, \\
\text{PH$_2$(adi)}+H & \rightarrow \text{PH$_3$.} 
\end{align*}
\]

Here, PH(adi) and PH$_2$(adi) represent adsorbed species on solid surfaces. The production process of H atoms, process (1), should be rate-determining. In addition, once PH(adi) is produced, that must be reduced to PH$_3$ eventually. If this is not the case, the PH$_3$ density may not depend linearly on the H-atom density in the absence of phosphorus pellets. The Langmuir-Hinshelwood mechanism, such as PH$_2$(adi)+PH(adi) $\rightarrow$ P(adi)+PH$_3$, may not be important. If PH$_3$ is produced in this mechanism only, the PH$_3$ density must be proportional to the square of the H-atom density. Although red phosphorus has a fairly high vapor pressure under vacuum [31], direct reactions between phosphorus vapor and H atoms in the gas phase must be minor. According to our density functional theoretical calculations with B3LYP/6-31+G(d,p) [32], the reaction of P$_2$ and H to produce PH and P is 144 kJ mol$^{-1}$ endothermic.
PH$_3$ ejected from the solid surfaces may be oxidized to PH$_x$(0$\leq x \leq 2$) by H atoms present in the gas phase. According to our density functional theoretical calculations [32], the production of PH$_2$ and H$_2$ in the reaction of PH$_3$ and H is 108 kJ mol$^{-1}$ exothermic. The rate constant at room temperature has been measured to be 3.24×10$^{-12}$ cm$^3$ s$^{-1}$ [33]. The production processes of PH and P, such as PH$_2$+H $\rightarrow$ PH+H$_2$, are also exothermic. The PH$_x$(0$\leq x \leq 2$) thus produced may deposit on the chamber walls and be etched by H atoms to reproduce PH$_3$. The PH$_3$ density measured in the present study should be that under such chemical equilibrium.

Finally, the highest PH$_3$ density observed in the present system, 1.3×10$^{13}$ cm$^{-3}$, is more than or comparable to those in many catalytic (hot-wire) [1-9] and plasma-enhanced [9-19] chemical vapor deposition processes. In other words, the amount of PH$_3$ produced by this technique may be enough for use in industrial applications.
References


Figure Captions

Figure 1. Mass spectrum of PH$_3$, (a), and those observed in P/H$_2$ systems, (b), (c), and (d). The total pressure was 40 Pa in all cases.
(a) PH$_3$ partial pressure was 0.11 Pa and the catalyst was not heated.
(b) H$_2$ flow rate was 100 sccm and the catalyst temperature was 2570 K.
(c) H$_2$ flow rate was 100 sccm and the catalyst temperature was 2340 K.
(d) H$_2$ flow rate was 100 sccm and the catalyst temperature was 1930 K.

Figure 2. Catalyst temperature dependence of H (●) and PH$_3$ (○) densities. The pressure and the flow rate of H$_2$ were 40 Pa and 100 sccm, respectively.
Fig. 1 (H. Umemoto et al)
Fig. 2 (H. Umemoto et al)