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Catalytic Decomposition of PH₃ on Heated Tungsten Wire Surfaces

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The catalytic decomposition processes of PH₃ on heated tungsten surfaces were studied to clarify the mechanisms governing phosphorus doping into silicon substrates. Mass spectrometric measurements show that PH₃ can be decomposed by more than 50% over 2000 K. H, P, PH, and PH₂ radicals were identified by laser spectroscopic techniques. Absolute density measurements of these radical species, as well as their PH₃ flow rate dependence, show that the major products on the catalyst surfaces are P and H atoms, while PH and PH₂ are produced in secondary processes in the gas phase. In other words, catalytic decomposition, unlike plasma decomposition processes, can be a clean source of P atoms, which can be the only major dopant precursors. In the presence of an excess amount of H₂, the apparent decomposition efficiency is small. This can be explained by rapid cyclic reactions including decomposition, deposition, and etching to reproduce PH₃.

1. Introduction

PH_3 is one of the most important dopant gases in the semiconductor industry; it is used not only in plasma-enhanced chemical vapor deposition (CVD) processes¹⁻¹¹⁾ but also in catalytic (hot-wire) CVD processes.¹¹⁻²⁰⁾ Recently, Hayakawa *et al.* have reported that phosphorus can be doped in crystalline silicon substrates by exposing the substrates to radical species produced in the catalytic decomposition of PH_3 or a mixture of PH_3 and H_2 on heated tungsten surfaces.^{12,13)} They have also demonstrated that this treatment can increase solar cell efficiency by reducing surface recombination rates at the interfaces between amorphous and crystalline silicon. In their studies, however, it is not clear what kinds of radical species are produced on heated tungsten surfaces, and the role of H_2 is also unclear. Now, it is well established that H atoms are produced efficiently on heated tungsten catalysts from H_2 .²¹⁾ H atoms may react with PH_3 to produce radical species in the gas phase.²²⁾ It is important to clarify which radical species are produced and how they contribute to the doping in this catalytic decomposition system.

As for the catalytic decomposition processes of another typical dopant gas, B_2H_6 , Comerford *et al.* measured the spatial distributions of B and H atoms and demonstrated that H-atom shifting reactions, $\text{BH}_x + \text{H} \leftrightarrow \text{BH}_{x-1} + \text{H}_2$, play key roles.²³⁾ This conclusion has been supported by the recent modeling studies of Mankelevich *et al.*²⁴⁾ It is important to ascertain whether similar H-shifting reactions play roles in PH_3/H_2 systems. In the catalytic decomposition of SiH_4 , it has been shown that Si is one of the major species produced directly on catalysts.²⁵⁻²⁹⁾ The direct production processes of SiH , SiH_2 , and SiH_3 are rather minor. In contrast, the main products in the decomposition of NH_3 are NH_2 and H .³⁰⁾ If this difference can be ascribed to the

difference in bond energies, since H-PH₂ bonds are still weaker than H-SiH₃ bonds, P and H atoms should be the only major species produced on the catalysts. In plasma-enhanced CVD processes of a mixture of PH₃ and H₂, the production of H, PH, and PH₂ radicals has been confirmed by optical emission spectroscopy, while P atoms have not been identified.³¹⁾ Thus, the major radical species in catalytic and plasma decomposition processes may be different.

In the present study, H, P, PH, and PH₂ radicals were identified by laser spectroscopic techniques, in both PH₃/He and PH₃/He/H₂ systems. The catalytic decomposition mechanisms of these systems are discussed based on the absolute density measurements of these radical species under various conditions.

2. Experimental Procedure

The experimental procedure and apparatus were similar to those described elsewhere.³²⁻³⁷⁾ Since PH₃ is toxic and explosive, a safe gas handling system supplied by Tomoe Shokai was employed. PH₃ diluted with He (or a mixture with H₂) was decomposed on a resistively heated tungsten wire installed in a cylindrical chamber evacuated by a turbomolecular pump (Osaka Vacuum TG220FCAB). Gas flow rates were controlled by mass flow controllers (Horiba STEC SEC-40M). The length and diameter of the W wire were 30 cm and 0.39 mm, respectively. The wire temperature was evaluated from its electric resistivity.

Mass spectrometric analyses were carried out to measure the PH₃ and H₂ densities. A quadrupole mass-spectrometer (Anelva M-QA200TS) was attached to the chamber through a sampling hole. The electron impact energy was 70 eV. The flight tube was differentially pumped down to 5×10^{-4} Pa with another turbo molecular pump (Osaka

Vacuum TG350FCWB). By measuring the peak heights of PH^+ ions, it was possible to evaluate the decomposition efficiencies of PH_3 at various catalyst temperatures. The absolute densities of H_2 were evaluated by comparing the H_2^+ mass signal with that when a known amount of H_2/He was flown.

The H-atom densities were evaluated by either vacuum-ultraviolet (VUV) laser absorption or VUV laser-induced fluorescence (LIF).²¹⁾ The distance between the catalyst and the laser beam detection zone was 6 cm. By using VUV laser absorption, it is possible to determine the absolute densities, while VUV-LIF is more sensitive. The laser wavelength was 121.6 nm in both techniques. A dye laser (Sirah CSTR-LG-18) pumped with a neodymium-doped yttrium aluminum garnet (Nd:YAG) laser (Quanta-Ray GCR-170) was used as a light source. The frequency of the dye laser output at 729.6 nm was doubled by a KH_2PO_4 (KDP) crystal and then tripled by a mixture of Kr and Ar. The resulting VUV light was collimated with a 100-mm focal-length MgF_2 lens. In the absorption measurements, the intensity after passing through the chamber was measured by monitoring the NO^+ ion current. In the VUV-LIF measurements, the induced fluorescence was detected with a solar-blind photomultiplier tube (Hamamatsu Photonics R6835) through an MgF_2 collimating lens and an interference filter (Acton Research 122-N). These signals were processed with a boxcar averager-gated integrator system (Stanford Research Systems SR240/SR250/SR280) or a digital oscilloscope (LeCroy 6051A).

To detect PH radicals, we employed an LIF technique around 338 nm, which corresponds to the (0,0) band of the $\text{A } ^3\Pi_i - \text{X } ^3\Sigma^-$ transition. The output of a dye laser was doubled in frequency by a KDP crystal installed in an autotracker (Inrad Autotracker III). The induced fluorescence was detected with a photomultiplier tube

(Hamamatsu Photonics R212UH) through a glass band-pass filter (Toshiba UVD33S). A boxcar averager-gated integrator system was used when the spectra were recorded. The absolute density was evaluated by comparing the LIF intensity under saturated conditions with the intensity of Rayleigh scattering caused by Ar. The procedure was similar to that employed for the absolute density measurements of Si, SiH, NH, OH, and NH₂.^{26,30,32-34} In order to evaluate the effect of the quenching of the upper A ³Π_i state, the decay profiles of the induced fluorescence were recorded with a digital oscilloscope at various H₂ pressures.

PH₂ radicals were also detected by LIF. The laser and detection systems were similar to those used in the detection of PH, except that the autotracker was not used. The (040)-(000) band around 454 nm and the (030)-(000) band around 474 nm of the $\tilde{A}^2A_1 - \tilde{X}^2B_1$ system were employed. A dielectric filter (Sigma Koki DIF-BLE) was used to block blackbody radiation from the catalyst. The procedure for the absolute density measurements was similar to that for PH. The laser was polarized linearly by a Glan-laser prism.

In the detection of P atoms, only the VUV-LIF technique could be employed. VUV laser absorption was also tried, but the P-atom density was too low to be measured. The wavelengths, 178.8, 178.3, or 177.5 nm, correspond to the $3s^23p^24s\ ^4P_{1/2,3/2,5/2} - 3s^23p^3\ ^4S_{3/2}$ transitions. These laser pulses were produced by a four-wave mixing technique.^{32,38,39} Two dye lasers (Sirah CSTR-LG-18 and Quanta Ray PDL-3) were simultaneously pumped with a Nd:YAG laser (Quanta-Ray PRO-190). The output of one dye laser (PDL-3) was doubled in frequency with a β -BaB₂O₄ (BBO) crystal and the wavelength was tuned to 255.9 nm, which is resonant to the $5p^56p\ [5/2]_2 - 5p^6\ ^1S_0$ transition of Xe. The output of another dye laser (CSTR-LG-18) was tuned to 450.7,

453.8, or 459.0 nm. The pulse energies of the lasers were 0.8 and 2 mJ. The two laser beams were combined and made collinear at a beam combiner and were focused into a vessel filled with 13 kPa of Xe, using a 150-mm focal-length achromatic lens to produce VUV radiation. The induced fluorescence was detected with a solar-blind photomultiplier tube through an MgF₂ collimating lens and an interference filter (Acton Research 180-N).

H₂ (Japan Air Gases, 99.999%), PH₃ (Japan Air Gases, diluted with He to 2.0%), He (Japan Air Gases, 99.999%), Kr (Nihon Sanso, 99.995%), Ar (Japan Air Gases, 99.999%), Xe (Teisan, 99.995%), and NO (Nihon Sanso, 99%) were used from cylinders without further purification.

3. Results

3.1 Mass spectrometric measurements

Figure 1 shows the dependence of the mass signals of PH₃ and H₂ on catalyst temperature in the absence of a H₂ flow. It is clear that PH₃ is consumed efficiently at temperatures above 1500 K, but the mass signal for PH₃ levels off over 2000 K and then increases slightly. As for H₂, there is a peak around 2100 K. As will be discussed in §4.1, these temperature dependences suggest the presence of H₂ removal processes and PH₃ reproduction processes on the surfaces. We should note here that the leveling off of PH₃ cannot be attributed to the lack of available surface reaction sites on the catalyst, because the decomposition efficiency is only slightly dependent on the PH₃ flow rate. The densities of both PH₃ and H₂ were proportional to the PH₃/He flow rate at all catalyst temperatures. In the PH₃/He/H₂ system, the apparent decomposition efficiency was small. Radical species must also be produced in these systems, but

these species must be deposited on chamber walls with high efficiencies. The deposited species must be etched by H atoms produced from H_2 to reproduce PH_3 .^{31,37)} These processes must be in balance.

3.2 H-atom density measurements

It was possible to detect H atoms in the PH_3/He systems without a H_2 flow, but their density decreased with time for the first several minutes. This can be explained by the deposition of phosphorus compounds on the chamber walls. H atoms must react with phosphorus compounds on chamber walls and be consumed to produce PH_3 . The film deposition and etching were confirmed by mass spectrometric observation of PH_3 in the presence of a pure H_2 flow after PH_3 decomposition. After several minutes, the chamber walls are covered with enough phosphorus compounds and the H-atom density levels off. When measured under such conditions, the H-atom density increased almost linearly against the PH_3/He flow rate as shown in Fig. 2. The H-atom density also increased with the increase in the catalyst temperature. Figure 3 shows an Arrhenius plot; the logarithm of the H-atom density is plotted against the reciprocal of the catalyst temperature. The apparent activation energy is calculated to be $115 \pm 6 \text{ kJ mol}^{-1}$, a value which is much smaller than that observed in the production of H atoms from H_2 , 239 kJ mol^{-1} .^{21,40)} This may correspond to the weakness of the H- PH_2 bond compared to the H-H bond, but, as will be discussed in §4.1, the situation is not so simple.

In $PH_3/He/H_2$ systems, the H-atom density was much higher and decreased with an increased PH_3/He flow rate. The H-atom density decreased by a factor of 2 when 10 sccm of PH_3/He were introduced to the H_2 flow of 100 sccm. When the catalyst

temperature was 1710 K, the H-atom density decreased from 4.8×10^{11} to $2.4 \times 10^{11} \text{ cm}^{-3}$ with the introduction of $8.2 \times 10^{12} \text{ cm}^{-3}$ of PH_3 . This decrease is much smaller than that observed in SiH_4/H_2 systems, in which the H-atom density decreased from 1.5×10^{14} to $7 \times 10^{12} \text{ cm}^{-3}$ with the addition of $1.8 \times 10^{13} \text{ cm}^{-3}$ of SiH_4 .⁴⁰⁾ In that system, the amount of H atoms removed was more than the amount of SiH_4 introduced and we have proposed to include a cyclic process to remove H atoms on the chamber walls. In the present system, it is not necessary to include such a process and it is possible to account for the decrease simply by assuming reactions between H and PH_3 in the gas phase. The rate constant for $\text{H} + \text{PH}_3 \rightarrow \text{H}_2 + \text{PH}_2$ has been reported to be $3.2 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ at room temperature.²²⁾ The rate constant must still be larger near the heated catalyst. Of course, poisoning of the catalyst surfaces may contribute to the decrease in the H-atom density.

3.3 LIF measurements of PH radicals

The LIF spectrum of the (0,0) band of the $\text{A } ^3\Pi_i - \text{X } ^3\Sigma^-$ transition of PH could be recorded between 337.5 and 339.7 nm. Figure 4 shows the result recorded in the presence of 20 sccm of H_2 and 10 sccm of PH_3/He , under the conditions that signal intensity was proportional to laser intensity. The total pressure was 4.1 Pa while the catalyst temperature was 2150 K. Since the laser pulse energy depended little on the wavelength in this region, no corrections were made. This spectrum can be reproduced by assuming a rotational temperature of 300 K. This temperature, which will be used to evaluate the absolute densities, may seem a little too low, since the temperatures for NH, SiH, OH, OD, and CN are between 350 and 500 K,^{26,30,32,34,41)} but in fact the choice of temperature has a rather minor effect on the absolute density

evaluation, as will be discussed later in this section. In the rotational population analysis, the spectroscopic assignments given by Pearce and coworkers^{42,43)} and the line strengths calculated by Budo⁴⁴⁾ were employed. It should be noted that predissociation is minor when the rotational quantum number is less than 11.^{45,46)}

In PH₃/He systems without a H₂ flow, the PH signals were weak and could be observed only when the catalyst temperature was higher than 2360 K and the PH₃/He flow rate was more than 60 sccm, which corresponds to a PH₃/He pressure of 8.5 Pa. The Arrhenius plot, shown in Fig. 5 by triangles, was almost linear and the activation energy was 171 ± 9 kJ mol⁻¹. This value is larger than that observed for the production of H atoms, 115 ± 6 kJ mol⁻¹. Figure 6 illustrates the dependence of the PH signal on the PH₃/He flow rate; the signal increased in proportion to the cube of the flow rate. This nonlinear dependence is similar to that observed in the catalytic production of NH from NH₃^{30,36)} and suggests the multistep production of PH. This point will be discussed in §4.1.

In PH₃/He/H₂ systems, the PH density increased almost linearly against the H₂ flow rate. The PH density also increased with an increase in the PH₃/He flow rate, but in this case, the plot showed saturation at high flow rates. The H₂ pressure dependence cannot be ascribed to the change in total pressure. In these measurements, the total pressure was not kept constant and the pressure broadening of the spectral lines, as well as the changes in diffusion rates, may have affected the results. No such increases, however, could be observed when He was introduced instead of H₂. The Arrhenius plots are illustrated in Fig. 5 by circles. The plots are not linear, especially at temperatures above 2500 K. This saturation at high temperatures can be explained by the overproduction of H atoms. In this system, H atoms are produced efficiently from

H₂ and gas-phase reactions to produce PH, such as PH₃+H→PH₂+H₂ and PH₂+H→PH+H₂, must take place. At 2270 K, the H-atom density in the absence of PH₃ is expected to be 2×10¹³ cm⁻³ which is more than the PH₃ density; 6.6×10¹² cm⁻³ when the PH₃/He flow rate is 10 sccm.

The temporal profiles of the induced fluorescence were measured as a function of H₂ pressure. This step was necessary to evaluate the quantum yield for the fluorescence which is needed to determine the absolute densities. The decay rate increased linearly with the H₂ pressure and the rate constant for the quenching of PH(A³Π_i, ν'=0), as well as the radiative lifetime, were evaluated. The results, 7.9×10⁻¹¹ cm³ s⁻¹ and 450 ns, are in fair agreement with the literature values.⁴⁷⁻⁴⁹ At a H₂ flow rate of 20 sccm, the H₂ density is 6.6×10¹⁴ cm⁻³ and 2% of PH(A³Π_i, ν'=0) is quenched. Quenching by PH₃ can be ignored because of its low pressure, although the rate constant is larger than that for H₂.⁴⁷⁾

The absolute density of PH(X ³Σ⁻) was evaluated by comparing the LIF intensity under saturated conditions with the intensity of Rayleigh scattering caused by Ar.^{26,30,32-34)} During the laser pulse, since the duration time of the laser is just 5 ns, collisional quenching or rotational state mixing can be ignored. Emission *via* off-diagonal transitions also was ignored since it is much weaker in the (0,1) band than in the (0,0) band.⁵⁰⁾ The ratio of the time integrated LIF intensity for the R₃₂(N''=3, J''=3) transition at 338.6 nm, *I*_{LIF}, to the intensity of Rayleigh scattering caused by Ar, *I*_R, was 1.7 when the PH₃/He flow rate, H₂ flow rate, catalyst temperature, and Ar density were 10 sccm, 20 sccm, 2220 K, and 1.6×10¹⁸ cm⁻³, respectively. Here, *J*'' represents the total angular momentum quantum number exclusive of nuclear spin and *N*'' that exclusive of nuclear and electron spin. The above ratio should be given by:

$$\frac{I_{\text{LIF}}}{I_{\text{R}}} = \frac{S_{\text{L}}}{N_0 \sigma E_{\text{L}}} \frac{h\nu}{4\pi} \phi N^*,$$

where N_0 is the Ar density, S_{L} is the cross section of the laser beam, 0.020 cm^2 , σ is the differential cross section for Rayleigh scattering, $3.1 \times 10^{-27} \text{ cm}^2$, E_{L} is the laser pulse energy in the Rayleigh scattering measurements, 0.20 mJ , $h\nu$ is the photon energy, ϕ is the quantum yield of the fluorescence, and N^* is the number density of excited PH radicals. As has been mentioned, since the quenching processes of $\text{PH}(\text{A } ^3\Pi_i)$ by H_2 and PH_3 are minor, the quantum yield, ϕ , may be assumed to be unity. Under saturated conditions, the ratio of the population of the upper state, $\text{PH}(\text{A } ^3\Pi_i, v'=0, N'=5, J'=4)$, to that of the lower state, $\text{PH}(\text{X } ^3\Sigma^-, v''=0, N''=3, J''=3)$, before excitation is $1/2$ when the excitation laser is linearly polarized.⁵¹⁾ When a Boltzmann distribution at 300 K is assumed, the ratio of the population of the lower level of the $\text{R}_{32}(N''=3, J''=3)$ transition to the total population is 0.057 . Production of vibrationally excited PH may be minor judging from the absence of vibrationally excited hydride radicals in the catalytic decomposition of SiH_4 , NH_3 , and H_2O .^{26,30,34)} Taking into account all these factors, the total population of PH was calculated to be $6.2 \times 10^{10} \text{ cm}^{-3}$. A similar result was obtained when the $\text{R}_{32}(N''=2, J''=2)$ line was used. Since there are many correction terms, uncertainty by a factor of two may be unavoidable. The error caused by the uncertainty in the rotational temperature is less than this. When the rotational temperature is assumed to be 400 K , the total population is calculated to be $7.3 \times 10^{10} \text{ cm}^{-3}$.

3.4 LIF measurements of PH_2 radicals

It was possible to detect PH_2 radicals through $(0v'_20)-(000)$ bands of the $\tilde{\text{A}} \text{ } ^2\text{A}_1 - \tilde{\text{X}} \text{ } ^2\text{B}_1$

system, where v'_2 is the bending quantum number up to 4. Among them, the signal was the strongest for $v'_2=4$. This should be because it has the largest Franck-Condon factor.⁵²⁾ In the present study, besides the (040)-(000) band, LIF measurements were also made on the (030)-(000) band to check the possible contribution of predissociation. Figure 7 shows the LIF spectrum for the (030)-(000) band. The spectrum was recorded in the presence of 100 sccm of PH₃/He and H₂ flows. The total pressure was 28 Pa and the catalyst temperature was 2270 K. Correction due to the wavelength dependence of the laser intensity was not necessary in this region. The rotational analyses have been carried out by Berthou *et al.*,⁵³⁾ but not all the rotational lines have been assigned.

In the absence of a H₂ flow, the PH₂ density increased in proportion to the square of the PH₃/He flow rate, as shown in Fig. 8. Linear dependences, on the other hand, were observed between the PH₂ density and the H₂ flow rate. These results are also consistent with the multistep production mechanism of PH₂, as for PH. Arrhenius plots similar to those for PH could be obtained. The activation energy for the production of PH₂ in the absence of a H₂ flow was 129 ± 5 kJ mol⁻¹. The non-linearity observed in the presence of a H₂ flow can be explained by the overproduction of H atoms.

To evaluate the quantum yield of the induced fluorescence, the temporal profiles of the fluorescence were measured as a function of H₂ pressure. From the H₂ pressure dependence, the rate constants for the quenching by H₂ were determined to be $(4.2 \pm 0.1) \times 10^{-10}$ and $(2.1 \pm 0.1) \times 10^{-10}$ cm³ s⁻¹ for the $v'_2=4$ and $v'_2=3$ levels, respectively. The radiative lifetimes were determined to be 0.65 ± 0.01 and 1.44 ± 0.02 μ s. The lifetime of the $v'_2=4$ level is shorter than that reported by Xuan and Margani⁵⁴⁾ (0.9-1.1

μs), longer than that given by Huie *et al.*⁵⁵⁾ (0.35 μs), and much shorter than that reported by Sam and Yardley⁵⁶⁾ (2.1 μs). The lifetime of the $v'_2=3$ level is shorter than those reported by these investigators, which range from 1.8 to 5 μs . The cause of these differences is not clear. The rate constant for the quenching of the $v'_2=4$ level by H_2 is a little larger than that reported by Huie *et al.*, $2.7 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$, while that for the $v'_2=3$ level is in good agreement with their value, $2.2 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$.

Huie *et al.* mentioned that the radiative lifetime of $\text{PH}_2(\tilde{\text{A}}^2\text{A}_1)$ decreases suddenly when v'_2 increases from 3 to 4,⁵⁵⁾ and referred to the possibility of the predissociation of $\text{PH}_2(\tilde{\text{A}}^2\text{A}_1, v'_2=4)$. On the other hand, no such vibrational level dependence of the radiative lifetime was observed by Sam and Yardley,⁵⁶⁾ nor do Xuan and Margani confirm the presence of predissociation.⁵⁴⁾ The radiative lifetime of $v'_2=4$ was shorter than those of $v'_2=0-3$, but the decrease was not sudden. In short, it is not clear if $\text{PH}_2(\tilde{\text{A}}^2\text{A}_1, v'_2=4)$ predissociates or not. In order to check this, we evaluated the absolute density not only through the (040)-(000) band, but also through the (030)-(000) band. In the LIF measurements through the (040)-(000) band, the intensity for the $^P P_{2,N-2}(3_{12}-4_{22})$ transition was monitored at 455.2 nm.⁵³⁾ The ratio of I_{LIF} to I_{R} was 2.6 when the PH_3/He flow rate, H_2 flow rate, catalyst temperature, and Ar density were 100 sccm, 100 sccm, 2240 K, and $6.7 \times 10^{18} \text{ cm}^{-3}$, respectively. The cross section of the laser beam was the same as that used in the PH measurements, 0.020 cm^2 . The differential cross section for Rayleigh scattering is $9.6 \times 10^{-28} \text{ cm}^2$, while the laser pulse energy in the Rayleigh scattering measurements was 0.07 mJ. The quantum yield, ϕ , is calculated to be 0.51 from the decay rate measurements. Quenching by PH_3 may be ignored.⁵⁴⁾ Under saturated conditions, the ratio of the population of the upper state, $\text{PH}_2(\tilde{\text{A}}^2\text{A}_1, v'_1 v'_2 v'_3=040, J'_{KaKc}=3_{12})$, to that of the lower state, $\text{PH}_2(\tilde{\text{X}}^2\text{B}_1, v''_1 v''_2$

$v''_3=000$, $J''_{KaKc}=4_{22}$), before excitation is 7/18 when the laser is linearly polarized.⁵¹⁾ When a Boltzmann distribution at 300 K is assumed, the ratio of the population of the lower level of this transition to the total is 0.0036. The rotational partition function was calculated using a formula given by Herzberg.⁵⁷⁾ The rotational constants given by Dixon were employed in this calculation.⁵⁸⁾ The statistical weights due to nuclear spin statistics, as well as the energy splittings caused by electron spin, were taken into account. The total population of PH₂ finally obtained was $2.3 \times 10^{12} \text{ cm}^{-3}$. In the LIF measurements through the (030)-(000) band, we monitored the intensity for the $^P P_{2,N-2}(3_{12}-4_{22})$ transition at 475.3 nm.⁵³⁾ The quantum yield in this system was determined to be 0.49 and the absolute density was $2.6 \times 10^{12} \text{ cm}^{-3}$. This value is a little larger than that obtained through the (040)-(000) band, but this difference may be regarded as within the error limit. We may conclude that predissociation is minor. Figure 9 summarizes the results for the catalyst temperature dependence of the radical densities in the absence of a H₂ flow. The results for PH and PH₂ are extrapolated to PH₃/He flow conditions of 10 sccm and a total pressure of 2.0 Pa.

The vibrational relaxation during the radiative lifetime of the upper states must be minor because the induced fluorescence decayed single exponentially. Since the radiative lifetime of PH₂($\tilde{A}^2A_1$) decreases with an increase in vibrational energy,⁵⁴⁾ the decay profile must become nonexponential if vibrational relaxation takes place efficiently before fluorescence. This conclusion is consistent with the small rate constants for the vibrational relaxation of PH₂($\tilde{X}^2B_1$) by He and H₂.^{59,60)} The vibrational relaxation of PH₂($\tilde{A}^2A_1$) by PH₃ has also been reported to be inefficient.⁵⁴⁾ The Franck-Condon factors for the off-diagonal transitions are small and transitions such as (040)-(140) may be ignored.⁵²⁾

3.5 Detection of P atoms

P-atom density in the absence of a H₂ flow was proportional to the PH₃/He flow rate, as shown in Fig. 10. The P-atom density also increased with an increase in catalyst temperature but the Arrhenius plots were not linear, as illustrated in Figs. 9 and 11. P-atom density increased with a H₂ flow rate below 5 sccm, but showed saturation over 5 sccm. This is in contrast to the PH and PH₂ densities, which increased linearly against the H₂ flow rate. The increase below 5 sccm may be ascribed to the production of PH₃ from H atoms and phosphorus compounds on chamber walls, since a similar increase could be observed even in the absence of a PH₃ flow. When the H₂ flow was greater than 10 sccm, the densities of P, PH, and PH₂ were comparable. Arrhenius plots in the presence of a H₂ flow were not linear, either, and were similar to those shown in Fig. 11.

The absolute density of P atoms was estimated from the imprisonment lifetime of P(3s²3p²4s ⁴P_{5/2}). When the total pressure was kept below 5 Pa, the decay of the LIF signal was nearly exponential and the decay time was around 10 ns, independent of catalyst temperature or PH₃/He flow rate. This suggests that the resonance radiation is not imprisoned. The observed decay time is consistent with the natural radiative lifetime of P(⁴P_{5/2}), 4.6 ns, and the time resolution of the apparatus, around 5 ns. The decay time depended little on the total pressure, either, when the catalyst temperature was kept below 2150 K. On the other hand, decay time increased up to 67 ns when the total pressure and the catalyst temperature were adjusted to 100 Pa and 2400 K. The flow rates of PH₃/He and H₂ were both 20 sccm. This increase in the decay time must be ascribed to radiation imprisonment. The relationship between optical density and

imprisonment lifetime under high opacity conditions has been presented by Holstein.^{61,62)} If we assume an infinite cylinder geometry with a radius of 5 cm and a Doppler profile at 300 K, the above imprisonment lifetime, 67 ns, can be reproduced when the P-atom density is $2.2 \times 10^{12} \text{ cm}^{-3}$. In this calculation, the P-atom distribution was assumed to be uniform and the absorption coefficient at the center of the resonance line, k_0 , was multiplied by 0.79 considering the hyperfine structure.^{63,64)} The estimated P-atom density when the PH₃/He flow rate, H₂ flow rate, total pressure, and the catalyst temperature are 10 sccm, 0 sccm, 2.0 Pa, and 2050 K is $1 \times 10^{10} \text{ cm}^{-3}$, which is comparable to the H-atom density under the same conditions, $4 \times 10^9 \text{ cm}^{-3}$, but much higher than the densities of PH and PH₂. A similar conclusion was obtained when the H₂ flow rate was halved to 10 sccm, suggesting that the quenching effect by H₂ on the imprisonment lifetime of P(⁴P_{5/2}) is minor.

4. Discussion

4.1 Reaction kinetics

The nonlinear dependence of the PH and PH₂ densities on the PH₃/He flow rate, as well as their linear H₂ flow rate dependences, suggests that there is minor direct production of these species on catalyst surfaces. The major products are P and H atoms. The activation energy needed to produce H atoms in PH₃/He systems, $115 \pm 6 \text{ kJ mol}^{-1}$, is in fair agreement with that to produce PH₂ radicals, $129 \pm 5 \text{ kJ mol}^{-1}$, but the activation energy for PH radicals is larger, $171 \pm 9 \text{ kJ mol}^{-1}$. These results, together with those of the PH₃/He flow rate dependence of the radical densities, can be explained, at least qualitatively, by the following simple, multi-step, PH_x production mechanism:

Reverse processes, such as $\text{PH}_2 + \text{H}_2 \rightarrow \text{PH}_3 + \text{H}$, were not included because of their large endothermicities. The reproduction of PH_3 on surfaces was included to explain not only the presence of PH_3 in the absence of a PH_3 flow, but also the minor dependence of the PH_3 density, $[\text{PH}_3]$, on catalyst temperatures over 2000 K. A similar process has also been assumed in NH_3 systems.³⁰⁾ PH_3 may decompose to produce $\text{P} + \text{H} + \text{H}_2$, but for simplicity this process was not included. Under steady-state conditions,

$$\frac{d[\text{PH}_2]}{dt} = 0 = k_2[\text{H}][\text{PH}_3] - k_3[\text{PH}_2] - k_4[\text{H}][\text{PH}_2], \quad (11)$$

$$\frac{d[\text{PH}]}{dt} = 0 = k_4[\text{H}][\text{PH}_2] - k_5[\text{PH}] - k_6[\text{H}][\text{PH}], \quad (12)$$

$$\frac{d[\text{P}]}{dt} = 0 = k_1[\text{PH}_3] + k_6[\text{H}][\text{PH}] - k_7[\text{P}]. \quad (13)$$

Here, the rate constant for Reaction (i) is represented by k_i . The spatial distributions of gaseous species are assumed to be uniform and rate constants for surface reactions, such

as k_1 and k_3 , include the surface/volume ratio.

The above equations can be solved:

$$[\text{PH}_2] = \frac{k_2[\text{H}][\text{PH}_3]}{k_3 + k_4[\text{H}]}, \quad (14)$$

$$[\text{PH}] = \frac{k_2 k_4 [\text{H}]^2 [\text{PH}_3]}{(k_3 + k_4[\text{H}])(k_5 + k_6[\text{H}])}, \quad (15)$$

$$[\text{P}] = \frac{k_1[\text{PH}_3]}{k_7} + \frac{k_2 k_4 k_6 [\text{H}]^3 [\text{PH}_3]}{(k_3 + k_4[\text{H}])(k_5 + k_6[\text{H}])k_7}. \quad (16)$$

The dependence of $[\text{PH}_2]$ on catalyst temperature as well as that on the PH_3/He flow rate can be explained if $k_3 \gg k_4[\text{H}]$. In this case, $[\text{PH}_2]$ should be given by

$$[\text{PH}_2] = \frac{k_2[\text{H}][\text{PH}_3]}{k_3}. \quad (17)$$

In PH_3/He systems, mass spectroscopic measurements show that $[\text{PH}_3]$ is proportional to the PH_3/He flow rate even when the catalyst is heated, while it is almost catalyst temperature independent over 2000 K. It has also been shown that $[\text{H}]$ is proportional to the PH_3/He flow rate and has an Arrhenius-type temperature dependence. Then, $[\text{PH}_2]$ should be proportional to the square of the PH_3/He flow rate and should have the same temperature dependence as $[\text{H}]$, if k_2 and k_3 are catalyst temperature independent. The gas temperature near the catalyst may depend on its temperature, but that may decrease sharply with increased distance.

A similar discussion is possible for PH . The linear relationship between $[\text{PH}]$ and the cube of the PH_3/He flow rate in the absence of a H_2 flow can be derived if $k_5 \gg k_6[\text{H}]$, in addition to $k_3 \gg k_4[\text{H}]$. Equation (15) can be simplified to

$$[\text{PH}] = \frac{k_2 k_4 [\text{H}]^2 [\text{PH}_3]}{k_3 k_5}. \quad (18)$$

In this case, the activation energy for the production of PH must be twice that needed for the production of H . According to the present results, the ratio is 1.5. This should

be the limitation of the present simplified model, although the difference between 1.5 and 2 may not be critical, as shown in Fig. 9.

[P] is proportional to the PH₃/He flow rate. Then, the second term in eq. (16) must be ignored. This is reasonable if $k_3 \gg k_4[H]$ and $k_5 \gg k_6[H]$. The densities of P in the absence of a H₂ flow should be given by

$$[P] = \frac{k_1[PH_3]}{k_7}. \quad (19)$$

In the catalytic decomposition of NH₃, we have assumed a process to produce NH from adsorbed NH₂ and H on catalyst surfaces.³⁶⁾ Similar processes, such as PH₂+H→PH+H₂ and PH+H→P+H₂ may also take place on the catalyst surfaces. However, as will be discussed in §4.2, these processes are much more exothermic than NH₂+H→NH+H₂, and may take place more easily in the gas phase.

The catalyst temperature dependence of [P] is non-Arrhenius. Similar non-Arrhenius temperature dependences have been observed in the production of Si atoms from SiH₄ and some organic silicon compounds.^{29,65,66)} The curvature in the Arrhenius plot cannot be ascribed to the exhaustion of PH₃, because the saturation curves were very similar when the PH₃/He flow rate was changed between 5 and 20 sccm, as shown in Fig. 11. Duan *et al.* have proposed a decomposition model of SiH₄, in which the low temperature regime is reaction rate limited while the high temperature regime is dominated by mass transfer limitations.^{29,65)} A similar model may also be possible in the production of P atoms. Since k_7 may not change greatly with catalyst temperature, the catalyst temperature dependence of [P] may agree with that of k_1 . It should be noted that the catalyst temperature dependence of [H] may not necessarily represent that of k_1 , because there are many processes for the consumption and production of H atoms other than reaction (1), such as reactions (8), (9), and (10).

4.2 Energetics and symmetry considerations

As discussed in §4.1, the major products on the catalyst surfaces are P and H atoms and the direct production of PH and PH₂ is minor. This can be accounted for by the weak H-PH_x bond energies. According to our density functional calculations by a Gaussian09 program,⁶⁷⁾ the H-PH₂, H-PH, and H-P bond energies are 332, 316, and 303 kJ mol⁻¹, respectively. In these calculations, the geometry optimization as well as the potential-energy and the zero-point-energy evaluations were carried out at the B3LYP/6-31+G(d,p) level of theory. These calculated values are smaller than those for both H-NH_x and H-SiH_x.

P, PH, and PH₂ may be produced efficiently in the following H-atom shifting reactions in the presence of an excess amount of H₂:

These processes are similar to those in BH_x systems.²³⁾ The reverse processes in the gas phase may be ignored because of their large endothermicities. The following processes may also be ignored because of their endothermicities:

Reactions (20) and (21) are symmetry-forbidden under C_s symmetry.^{56,68)} However, the pre-exponential factor for reaction (20) has been reported to be nearly gas kinetic.²²⁾ In other words, reaction (20) must proceed under C₁ symmetry. Reaction (21) may proceed similarly.

5. Conclusions

The major products in the catalytic decomposition of PH_3 on heated tungsten surfaces are P and H atoms. PH and PH_2 radicals are also produced in the gas phase, but their densities are much lower, unless H_2 is introduced. In the presence of an excess amount of H_2 , the P, PH, and PH_2 densities become comparable. Very recently, Hayakawa has reported that the carrier density of a silicon substrate exposed to the radical species produced by the catalytic decomposition of PH_3 without H_2 dilution is higher than that exposed to the radicals with H_2 dilution.⁶⁹⁾ This difference may be related to the difference in the radical species present. Our study indicates that P atoms could be better dopant precursors in silicon than PH and PH_2 radicals. Since such selective radical production is difficult in plasma processes, catalytic decomposition must be more useful in phosphorus doping.

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Figure Captions

Fig. 1. Dependence of PH_3 and H_2 density on catalyst temperature in the absence of a H_2 flow. Circles represent the results for PH_3 , while triangles represent those for H_2 . The flow rates and pressures were 20 sccm and 3.5 Pa for open symbols and 10 sccm and 2.0 Pa for closed symbols.

Fig. 2. H-atom density as a function of PH_3/He flow rate measured by a VUV-LIF technique. H_2 was not added and the PH_3/He pressure at 17.5 sccm was 3.1 Pa. The inner walls of the chamber were covered with phosphorus compounds. The catalyst temperature was 2150 K.

Fig. 3. H-atom density as a function of the reciprocal of catalyst temperature, T_{cat} , in the absence of a H_2 flow, measured by a VUV-LIF technique. The flow rate and the pressure of PH_3/He were 10 sccm and 2.0 Pa, respectively. The absolute values were determined by a VUV absorption technique.

Fig. 4. Laser-induced fluorescence spectrum of PH ($\text{A } ^3\Pi_i, v'=0 - \text{X } ^3\Sigma^-, v''=0$). The flow rates of H_2 and PH_3/He were 20 and 10 sccm, respectively. The total pressure was 4.1 Pa. The catalyst temperature was 2150 K. The numbers are the total angular momentum quantum numbers exclusive of nuclear and electron spin.

Fig. 5. PH -radical densities as a function of the reciprocal of the catalyst temperature, T_{cat} . Circles represent the results in the presence of a 20 sccm flow of H_2 while the

triangles represent the results in its absence. The flow rates of PH₃/He were 20 (●), 10 (○), and 60 (▲) in sccm. The corresponding total pressures were 5.5, 4.1, and 8.5 Pa, respectively.

Fig. 6. PH-radical density as a function of the cube of the PH₃/He flow rate. The catalyst temperature was 2380 K and the total pressure at 100 sccm was 12 Pa.

Fig. 7. Laser-induced fluorescence spectrum of PH₂ ($\tilde{A}^2A_1, 030 - \tilde{X}^2B_1, 000$). The flow rates of H₂ and PH₃/He were both 100 sccm. The total pressure was 28 Pa. The catalyst temperature was 2270 K. The arrow shows the rotational line used for the absolute density measurement.

Fig. 8. PH₂-radical density as a function of the square of the PH₃/He flow rate. The catalyst temperature was 2580 K and the total pressure at 100 sccm was 12 Pa.

Fig. 9. Catalyst temperature dependence of P (■), H (□), PH₂ (●), and PH (○) densities in the absence of a H₂ flow. Results for H atoms are direct measurements while those for PH and PH₂ are extrapolated to the PH₃/He flow conditions of 10 sccm (2.0 Pa). The absolute densities of P atoms are just estimates. The dashed line represents a plot with an activation energy of 230 kJ mol⁻¹, twice that for H.

Fig. 10. P-atom density as a function of PH₃/He flow rate in the absence of a H₂ flow. The catalyst temperature was 2050 K. The pressure at 10 sccm was 2.0 Pa.

Fig. 11. P-atom densities as a function of the reciprocal of catalyst temperature in the absence of a H₂ flow. PH₃/He flow rates were 20, 15, 10, and 5 sccm from top to bottom.

Fig. 1.

Fig. 2.

Fig. 3.

Fig. 4.

Fig. 5.

Fig. 6.

Fig. 7.

Fig. 8.

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Fig. 10.

Fig. 11.