In-situ production of PH₃ from red phosphorus and atomic hydrogen

著者	Umemoto Hironobu, Nishihara Yushin, Ishikawa Takuma
journal or publication title	Chemical Physics Letters
volume	514
number	1-3
page range	26-28
year	2011-09-27
出版者	Elsevier
権利	(C) 2011 Elsevier B.V. All rights reserved.
URL	http://hdl.handle.net/10297/6162

doi: 10.1016/j.cplett.2011.08.014

***In-situ* production of PH₃ from red phosphorus and atomic hydrogen**

Hironobu Umemoto^{a,b,*}, Yushin Nishihara^{a,b}, Takuma Ishikawa^{a,b}

^a *Faculty of Engineering, Shizuoka University, Johoku, Naka, Hamamatsu, Shizuoka 432-8561, Japan*

^b *Japan Science and Technology Agency, CREST, 5, Sanbancho, Chiyoda, Tokyo 102-0075, Japan*

* Corresponding author. Tel.: +81 53 478 1275; Fax: +81 53 478 1275.

E-mail address: thumemo@ipc.shizuoka.ac.jp (H. Umemoto).

Abstract

The production of PH₃ from red phosphorus and the atomic hydrogen formed in the catalytic decomposition of H₂ on heated W surfaces was confirmed. The absolute density of the PH₃ could be as high as 10¹³ 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 PH₃ molecule, but showed minor dependence on the amount of red phosphorus. These results suggest that the rate-determining step for the production of PH₃ is that which produces H atoms.

1. Introduction

PH₃ 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 PH₃ 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 PH₃ from phosphorus vapor, possibly P₂ and P₄, 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 PH₃ from H atoms and solid phosphorus deposited on chamber walls [21]. However, no quantitative analyses have been made for this PH₃ production process. The absolute density of PH₃ has not been evaluated, either.

In the present study, we tried to produce PH₃ in a reaction between solid red phosphorus and the atomic hydrogen formed in the catalytic decomposition of H₂. It is now well established that H atoms can be produced efficiently from H₂ on heated W catalysts [22]. The absolute densities of H atoms and PH₃ were measured to obtain information on the PH₃ 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 H₂ on a heated W wire installed in a chamber evacuated with a turbomolecular pump. The pressure and the flow rate of H₂ were kept constant at 40 Pa and 100 sccm (1sccm=6.9×10⁻⁷ 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.

PH₃ 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 PH₃, diluted with He and H₂, 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- α absorption measurements at 121.6 nm [22].

H₂ (Japan Air Gases, 99.999%) and PH₃ (Japan Air Gases, diluted with He to 2.0%) were used from cylinders without further purification. The purity of the PH₃ 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 H₂ and red phosphorus. This figure also includes a mass spectrum of PH₃, recorded without heating the W wire. The similarity in the mass patterns confirms the production of PH₃ from H atoms and red phosphorus. The peak intensity ratio corresponding to the mass numbers of 31, 32, 33, and 34 for PH₃ 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 $2 \times 10^{12} \text{ cm}^{-3}$. The PH₃ density when the catalyst temperature was 2570 K was evaluated to be as high as $1.3 \times 10^{13} \text{ cm}^{-3}$. 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 $215 \pm 7 \text{ kJ mol}^{-1}$, 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:

Here, PH(ad) and $\text{PH}_2(\text{ad})$ represent adsorbed species on solid surfaces. The production process of H atoms, process (1), should be rate-determining. In addition, once PH(ad) 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 $\text{PH}_2(\text{ad}) + \text{PH(ad)} \rightarrow \text{P(solid)} + \text{PH}_3$, 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 $\text{PH}_x(0 \leq x \leq 2)$ 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 $3.24 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ [33]. The production processes of PH and P, such as $\text{PH}_2 + \text{H} \rightarrow \text{PH} + \text{H}_2$, are also exothermic. The $\text{PH}_x(0 \leq x \leq 2)$ 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, $1.3 \times 10^{13} \text{ cm}^{-3}$, 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

- [1] T. Hayakawa, M. Miyamoto, K. Koyama, K. Ohdaira, H. Matsumura, *Thin Solid Films* 519 (2011) 4466.
- [2] I.T. Martin, H.M. Branz, P. Stradins, D.L. Young, R.C. Reedy, C.W. Teplin, *Thin Solid Films* 517 (2009) 3496.
- [3] P. Kumar, B. Schroeder, *Thin Solid Films* 516 (2008) 580.
- [4] S.A. Filonovich, M. Ribeiro, A.G. Rolo, P. Alpuim, *Thin Solid Films* 516 (2008) 576.
- [5] S. Miyajima, A. Yamada, M. Konagai, *Jpn. J. Appl. Phys.* 46 (2007) 1415.
- [6] Q. Zhang, M. Zhu, F. Liu, J. Liu, *Thin Solid Films* 501 (2006) 141.
- [7] S.B. Patil, A.V. Vairagar, A.A. Kumbhar, L.K. Sahu, V. Ramgopal Rao, N. Venkatramani, R.O. Dusane, B. Schroeder, *Thin Solid Films* 430 (2003) 63.
- [8] S.R. Jadkar, J.V. Sali, M.G. Takwale, D.V. Musale, S.T. Kshirsagar, *Thin Solid Films* 395 (2001) 206.
- [9] S.A. Filonovich, P. Alpuim, L. Rebouta, J.-E. Bourée, Y.M. Soro, *J. Non-Cryst. Solids* 354 (2008) 2376.
- [10] N. Yoshida, S. Terazawa, A. Takeuchi, N. Yoneyama, T. Morino, Z. Jun, H. Natsuhara, S. Nonomura, *Physica Status Solidi C* 7 (2010) 790.
- [11] C. Jeong, S. Boo, T.-W. Kim, B.-H. Choi, H.-S. Kim, C.-R. Chang, J.-H. Lee, K. Kamisako, *J. Nanosci. Nanotechnol.* 8 (2008) 5521.
- [12] H. Kato, H. Watanabe, S. Yamasaki, H. Okushi, *Diam. Relat. Mater.* 15 (2006) 548.
- [13] P. Alpuim, V. Chu, J.P. Conde, *J. Vac. Sci. Technol. A* 21 (2003) 1048.
- [14] S. Koizumi, M. Kamo, Y. Sato, S. Mita, A. Sawabe, A. Reznik, C. Uzan-Saguy, R. Kalish, *Diam. Relat. Mater.* 7 (1998) 540.

- [15] Y. Kuo, Appl. Phys. Lett. 71 (1997) 2821.
- [16] S. Yonekubo, K. Kamimura, Y. Onuma, Thin Solid Films 281-282 (1996) 159.
- [17] S. Thomas, J. Fretwell, D. Kinosky, R. Qian, A. Mahajan, P. Munguia, S. Banerjee, A. Tasch, C. Magee, J. Electro. Mater. 24 (1995) 183.
- [18] R.D. Knox, V. Dalal, B. Moradi, G. Chumanov, J. Vac. Sci. Technol. A 11 (1993) 1896.
- [19] H. Kakinuma, M. Mohri, T. Tsuruoka, Jpn. J. Appl. Phys. 31 (1992) L1392.
- [20] M. Naitoh, M. Umemo, Jpn. J. Appl. Phys. 26 (1987) L1538.
- [21] M. Naitoh, T. Soga, T. Jimbo, M. Umemo, J. Cryst. Growth 93 (1988) 52.
- [22] H. Umemoto, Chem. Vapor Deposition 16 (2010) 275.
- [23] H. Umemoto, M. Moridera, J. Appl. Phys. 103 (2008) 034905.
- [24] H. Umemoto, H. Kusanagi, Open Chem. Phys. J. 2 (2009) 32.
- [25] H. Umemoto, H. Kusanagi, K. Nishimura, M. Ushijima, Thin Solid Films 517 (2009) 3446.
- [26] M. Yamamoto, T. Maruoka, A. Kono, H. Horibe, H. Umemoto, Appl. Phys. Express 3 (2010) 026501.
- [27] M. Yamamoto, T. Maruoka, A. Kono, H. Horibe, H. Umemoto, Jpn. J. Appl. Phys. 49 (2010) 016701.
- [28] Y. Nozaki, K. Kongo, T. Miyazaki, M. Kitazoe, K. Horii, H. Umemoto, A. Masuda, H. Matsumura, J. Appl. Phys. 88 (2000) 5437.
- [29] H. Umemoto, K. Ohara, D. Morita, Y. Nozaki, A. Masuda, H. Matsumura, J. Appl. Phys. 91 (2002) 1650.
- [30] H. Umemoto, K. Ohara, D. Morita, T. Morimoto, M. Yamawaki, A. Masuda, H. Matsumura, Jpn. J. Appl. Phys. 42 (2003) 5315.
- [31] H.W. Melville, S.C. Gray, Trans. Faraday Soc. 32 (1936) 1026.
- [32] Gaussian 09, Revision B.01, M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A.

Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A. Montgomery, Jr., J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, O. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, D.J. Fox, Gaussian, Inc., Wallingford CT, 2010.

[33] N.L. Arthur, I.A. Cooper, *J. Chem. Soc. Faraday Trans.* 93 (1997) 521.

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)