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<th>Catalytic decomposition of phosphorus compounds to produce phosphorus atoms</th>
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Vacuum-ultraviolet laser-induced fluorescence identified atomic phosphorus in the gas phase when phosphine, triethylphosphine, or molecular phosphorus sublimated from solid red phosphorus was decomposed on heated metal wire surfaces. Atomic phosphorus was found to be one of the major products in all systems, and its density increased monotonically with wire temperature but showed saturation at high temperatures. A wire material dependence of density was observed for molecular phosphorus, suggesting that the decomposition of the compound is catalytic. Electron probe microanalyzer (EPMA) measurement showed that the wires are not phosphorized when heated in the presence of phosphine or molecular phosphorus.
1. Introduction

Recently, we have studied the decomposition processes for PH\textsubscript{3} on heated metal wire surfaces by employing both laser spectroscopic and mass spectrometric techniques\textsuperscript{1,2).} It has been shown that PH\textsubscript{3} can be decomposed efficiently when the wire temperature is higher than 2000 K and that the major products on the wire surfaces are P and H atoms. P-atom density can be increased up to $4 \times 10^{10}$ cm\textsuperscript{-3} when the PH\textsubscript{3} pressure is 0.04 Pa\textsuperscript{1).} The P atoms thus produced can be dopant precursors for n-type silicon substrates\textsuperscript{3,4).} PH and PH\textsubscript{2} radicals could also be identified, but their densities were much less than that of P atoms in the absence of a H\textsubscript{2} flow. These species are produced in secondary reaction processes with H atoms in the gas phase\textsuperscript{1).} We have also reported that PH\textsubscript{3}, and consequently PH\textsubscript{x} ($x=0, 1, 2$) radicals, can be produced from red phosphorus and H atoms produced by the catalytic decomposition of H\textsubscript{2} on heated metal wire surfaces\textsuperscript{5).} In this case, it is possible to produce PH\textsubscript{x} radicals without using toxic and explosive gases in cylinders, but it is impossible to produce P atoms selectively. In the presence of an excess amount of H\textsubscript{2} flow, the densities of P, PH, and PH\textsubscript{2} are comparable\textsuperscript{1).}

In the present study, P atoms were produced by decomposing triethylphosphine, P(C\textsubscript{2}H\textsubscript{5})\textsubscript{3}, and molecular phosphorus, P\textsubscript{4}, sublimated from solid red phosphorus on heated metal wire surfaces, and the results were compared with that for PH\textsubscript{3}. It is useful if P atoms can be produced selectively without using toxic and explosive gases, such as PH\textsubscript{3}. P(C\textsubscript{2}H\textsubscript{5})\textsubscript{3} has been proposed as a phosphorus source in the preparation of InP epiwafer by thermal chemical vapor deposition\textsuperscript{6).} It has been reported that the efficiency of phosphorus supply can be improved using a mixture of P(C\textsubscript{2}H\textsubscript{5})\textsubscript{3} and PH\textsubscript{3}.

2. Experimental procedure
The experimental procedure and apparatus were similar to those described elsewhere.\textsuperscript{1,2)} Gaseous materials were introduced into a vacuum chamber through mass flow controllers to be decomposed on a resistively heated metal wire. The typical wire diameter was 0.39 mm, while the length was 30 cm. The wire temperature was ascertained from the wire electrical resistivity.\textsuperscript{7)} It was also checked with a two-wavelength thermometer (LumaSense Technologies ISR 12-LO). The agreement between the evaluated temperatures from the resistivity and the directly measured ones was satisfactory.

In the decomposition study of molecular phosphorus, a pellet of red phosphorus, 14 mm in diameter and 1 mm in thickness, was placed at the bottom of the vacuum chamber. The pellet could be heated with the thermal radiation from the heated metal wire. The distance between the metal wire and the phosphorus pellet was 10 cm.

P atoms were detected by a vacuum-ultraviolet (VUV) laser-induced fluorescence (LIF) technique. The distance between the wire and the P-atom detection zone was 6 cm. A four-wave mixing technique was used to produce laser pulses at 177.5 nm, which corresponds to the $3s^23p^24s\,^4P_{5/2} - 3s^23p^3\,^4S_{3/2}$ resonance transition. Xe was used as a nonlinear optical medium to produce the VUV radiation. The induced fluorescence was detected with a solar-blind photomultiplier tube through a MgF$_2$ collimating lens and an interference filter. The absolute densities of P atoms in the catalytic decomposition of PH$_3$ have been determined from the imprisonment lifetime of P($3s^23p^24s\,^4P_{5/2}$). The P-atom densities from other sources were evaluated by comparing the LIF signal intensity with that observed in the catalytic decomposition of PH$_3$ at 2250 K. At this temperature, the production of P atoms from sublimated
molecular phosphorus is minor even in the presence of a phosphorus pellet, while PH$_3$ can be decomposed efficiently to produce P atoms. In the spectrum measurement, the VUV laser wavelength was scanned between 177.2 and 179.1 nm.

As for P(C$_2$H$_5$)$_3$, mass spectrometric analysis, as well as the laser spectroscopic detection of PH and PH$_2$ radicals, was carried out. It is possible to evaluate the decomposition efficiencies of P(C$_2$H$_5$)$_3$ at various wire temperatures by measuring the mass spectral peak heights of the parent ions.

In order to examine the phosphorization of wires, W and Ta wires were exposed to PH$_3$/He or molecular phosphorus and then analyzed with an electron probe microanalyzer (Shimadzu EPMA-1600) to evaluate their P-atom content. The exposure time was 60 min, while the wire temperatures were 2800 K for W and 2500 K for Ta. The pressure of PH$_3$/He was 3.3 Pa (0.066 Pa of PH$_3$). The K$\alpha$ lines at 0.616 nm were used to identify the P atoms.

The red phosphorus used was a product of Kanto Kagaku and its purity was 98.0%. The P(C$_2$H$_5$)$_3$ used was a product of Tri Chemical Laboratories and diluted with He to 2.0% before use. PH$_3$ (Japan Air Gases, diluted with He up to 2.0%), Xe (Teisan, 99.995%), and He (Japan Air Gases, 99.999%) were used from cylinders without further purification. The W (99.95%), Ta (99.95%), and Mo (99.95%) wires used were products of Nilaco.

3. Results

3.1 Decomposition of molecular phosphorus

P atoms were easily detected when a metal wire was heated in the presence of a red phosphorus pellet. Figure 1 shows the laser-induced fluorescence spectra. The three
lines correspond to the transitions from the ground $3s^23p^34S_{3/2}$ state to the $3s^23p^24s\,^4P_{1/2}$, $^4P_{3/2}$, and $^4P_{5/2}$ states. Figure 1(a) shows the result when a W wire was heated at 2050 K in the presence of a mixture of H$_2$ and PH$_3$/He, while Fig. 1(b) shows the result when a Ta wire was kept at 2500 K in the presence of a red phosphorus pellet without a gas flow.

In Fig. 2, the P-atom density is plotted against the reciprocals of the W, Ta, and Mo wire temperatures in the absence of a gas flow. The results for PH$_3$ and P(C$_2$H$_5$)$_3$ are also plotted by open symbols. The lower P-atom densities for molecular phosphorus than for PH$_3$ may partly be ascribed to the lower vapor pressure of molecular phosphorus, as will be discussed later. The plots are nonlinear, that is, they are non-Arrhenius. Also note that, below 2500 K, the P-atom production efficiency for Ta is higher than those for W and Mo.

The signal intensity showed no change when He at 4.0 Pa was introduced, when the He flow rate was kept below 15 sccm (1 sccm = $6.9 \times 10^{-7}$ mol s$^{-1}$). This lack of change suggests that the difference between the Doppler widths of the spectral lines has only a minor effect on the LIF signal intensity. In the absence of He, since the vapor pressure of molecular phosphorus is low, P atoms may be translationally hot and the spectral line width may depend on the wire temperature. P atoms must be relaxed completely by the introduction of He at 4.0 Pa, since it has been shown that PH radials are completely thermalized when the total pressure is 4.0 Pa.$^{1}$ The wire length dependence was also examined. When the length of the W wire was changed from 30 to 50 cm, the P-atom density increased by a factor of 2.7, which is larger than the length ratio of 1.7. This can be explained by the increase not only in the wire surface area but also in the pellet temperature.
The surface temperature of the red phosphorus pellet, measured with a temperature-indicating label (Nichiyu Giken), increased with the wire temperature, although the dependence was rather weak. It was 410 K at a W wire (30 cm) temperature of 3000 K, while it was 390 K at 2250 K. The predominant molecular phosphorus at such temperatures is $P_4$. It has been reported that the evaporation of $P_2$ can be ignored below 1000 K. The vapor pressure of $P_4$ is estimated to be $\approx 0.01$ Pa at these temperatures.

3.2 Decomposition of $P(C_2H_5)_3$

Figure 2 also shows the results of the wire temperature dependence for $P(C_2H_5)_3$. The Arrhenius plot is not linear, either. The production efficiency of P atoms for $P(C_2H_5)_3$ is comparable to that for $PH_3$. The production of PH and $PH_2$ was minor in the absence of a H$_2$ flow, although the densities of both compounds increased with the H$_2$ pressure. In the presence of more than 5 Pa of H$_2$, the PH and $PH_2$ densities were comparable to those observed in the $PH_3$/He/H$_2$ systems. The P-atom density increased with the flow rate of $P(C_2H_5)_3$/He, as shown in Fig. 3, but it showed a rather weak dependence on the H$_2$ flow rate. Such a flow rate dependence suggests that P atoms are produced on wire surfaces directly, while PH and $PH_2$ radicals are formed in the reactions with H atoms produced from H$_2$. This is very similar to that observed in the $PH_3$ systems.

Mass spectrometric measurement showed that the decomposition efficiency of $P(C_2H_5)_3$ exceeds 80% when the W wire temperature is higher than 2000 K. This is in contrast to the decomposition of $PH_3$, whose decomposition efficiency saturates at $\approx 50\%$ at over 2000 K. As for the stable decomposition products, $PH_3$ could be
identified in addition to C₂H₆, H₂PC₂H₅, and HP(C₂H₅)₂.

Sugiyama et al. have demonstrated that the efficiency of phosphorus supply can be improved using a mixture of P(C₂H₅)₃ and PH₃.⁶ In our present measurement, however, no synergistic effect was observed in the production of P atoms when both P(C₂H₅)₃ and PH₃ were introduced.

3.3 EPMA analysis
The result of the EPMA analysis at the edge of a Ta wire exposed to molecular phosphorus is shown in Fig. 4. Similar results were obtained with exposure to PH₃, and for W wires. In all cases, no phosphorization was observed. The P-atom density should be less than the detection limit, i.e. 0.01% Ta or W. P atoms were not identified in the line profile analysis along the wire axis, either. These results are consistent with the absence of aging changes in the electric resistivity and the wire thickness, as well as in the catalytic activity.² On the other hand, when P(C₂H₅)₃ was used, carburization could not be avoided and the resistivity increased with the exposure time.

4. Discussion
First, it can be concluded that the decomposition of P₄ on heated metal surfaces is not thermal but catalytic in nature, since the wire temperature dependences of the P-atom density are completely different among different wire materials. Similar conclusions have been drawn in SiH₄ and PH₃ systems,²,¹⁰ but the present result is more remarkable. The smaller P-atom densities for P₄ than for PH₃ can partly be explained by the low vapor pressure of the former. In addition, note that in the decomposition of tetrahedral
P₄ to produce P atoms, three bonds must be broken simultaneously. This is in contrast to PH₃, for which stepwise dissociation is possible. According to our density functional calculations using the Gaussian09 program,¹¹ the production of P(^4S) and P₃(^4B₁) in the gas phase is endothermic with 529 kJ mol⁻¹. The production of two P₂(X ^1Σ⁺g⁺) molecules is less endothermic, with only 158 kJ mol⁻¹; however, in this case, four P-P bonds must be broken simultaneously. The total endothermicity for the P₄ → 2P+P₂ reaction is 605 kJ mol⁻¹. In these calculations, the geometry optimization as well as the potential-energy and zero-point-energy evaluations were carried out at the B3LYP/6-31+G(d,p) level of the theory.

In the decomposition of P₄, the saturation of the P-atom density at high wire temperatures should be explained by the mass-transport-limited model proposed in the decomposition of SiH₄ and PH₃.¹²,¹⁰,¹² In this model, the desorption processes for physisorbed parent molecules from catalyst surfaces back to the gas phase compete with the decomposition processes. In the decomposition of B₂H₆, Comerford et al. have reported that the B-atom density increases with the wire temperature up to 2370 K, but above this temperature the density saturates and even decreases.¹³ They explained these results by boron accommodation into the wire, based on secondary ion mass spectroscopic analysis. Similar processes of silicidation¹⁴⁻²¹ and carburization²¹⁻²⁴ of W wires have been observed, although silicidation is less remarkable at high wire temperatures. In the present phosphorus systems, however, phosphorization does not occur at any temperature. The absence of permanent phosphorization suggests that P atoms may leave the metal surfaces easily. The phosphorus vapor pressure must be too high for efficient accommodation into the metal wires.

An alternative explanation to the saturation of the P-atom densities is possible
for \( \text{P}(\text{C}_2\text{H}_5)_3 \); the depletion of the material gas. Similar mechanisms have been proposed in the catalytic decomposition of some organosilicon compounds.\(^{25,26}\) In the decomposition of \( \text{PH}_3 \), this mechanism cannot be applied since the decomposition efficiency saturates at \( \approx 50\% \).\(^{1,2}\) On the other hand, in the decomposition of \( \text{P}(\text{C}_2\text{H}_5)_3 \), the efficiency exceeds 80\% and this mechanism may also be applicable. The higher decomposition efficiency may be related to the smaller bond energy. According to our density functional calculations, the \((\text{C}_2\text{H}_5)_2\text{P}-\text{CH}_2\text{CH}_3\) bond energy is 242 kJ mol\(^{-1}\), which is much lower than that of \( \text{H}_2\text{P}-\text{H} \), 332 kJ mol\(^{-1}\). The \((\text{C}_2\text{H}_5)_3\text{P}-\text{CH}_2\text{CH}_3\) bond energy is also much lower than that for \((\text{CH}_3)_3\text{Si}-\text{CH}_3\), 344 kJ mol\(^{-1}\), and the ejection of physisorbed \( \text{P}(\text{C}_2\text{H}_5)_3 \) from hot wire surfaces is less likely.

5. **Conclusions**

\( \text{PH}_3 \), \( \text{P}_4 \), and \( \text{P}(\text{C}_2\text{H}_5)_3 \) can be decomposed efficiently on heated catalyst surfaces to produce \( \text{P} \) atoms. The \( \text{P} \) atoms thus produced can be good dopant precursors for preparing n-type silicon. The \( \text{P} \)-atom density obtained by the catalytic decomposition of \( \text{P}_4 \) was less than that for \( \text{PH}_3 \) under the same wire conditions, but it would be easy to increase the density by increasing the temperature of the red-phosphorus reservoir. As for \( \text{P}(\text{C}_2\text{H}_5)_3 \), the production efficiency of \( \text{P} \) atoms was comparable to that for \( \text{PH}_3 \), and the production of \( \text{PH} \) and \( \text{PH}_2 \) was minor in the absence of a \( \text{H}_2 \) flow. Although no phosphorization of wire materials occurs at any temperature, carburization cannot be avoided when \( \text{P}(\text{C}_2\text{H}_5)_3 \) is used.

**Acknowledgment**

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2) H. Umemoto, to be published in Thin Solid Films.


11) Gaussian 09, Revision B.01 (Gaussian, Wallingford, CT, 2010).


Figure captions

Fig. 1. Laser-induced fluorescence spectra of P atoms. The wire length and diameter were 30 cm and 0.39 mm, respectively. (a) In the presence of PH$_3$/He and H$_2$ flows. The flow rates were 10 and 20 sccm, respectively, while the total pressure was 4.1 Pa. The W wire temperature was 2050 K. (b) In the presence of a solid red phosphorus pellet without a gas flow. The Ta wire temperature was 2500 K.

Fig. 2. (Color online) Dependence of P-atom density on the wire temperature. The wire length and diameter were 30 cm and 0.39 mm, respectively. The wire and source materials were W/PH$_3$/He (□), W/P(C$_2$H$_5$)$_3$/He (○), W/P$_4$ (■), Ta/P$_4$ (▲), and Mo/P$_4$ (●). The PH$_3$/He pressure was 2.0 Pa, while the P(C$_2$H$_5$)$_3$/He pressure was 1.0 Pa.

Fig. 3. P-atom density as a function of P(C$_2$H$_5$)$_3$/He flow rate in the absence of a H$_2$ flow. The W wire temperature was 2520 K. The evacuation rate was kept constant and the P(C$_2$H$_5$)$_3$ partial pressure was almost proportional to the flow rate. The total pressure at 15 sccm was 3.0 Pa.

Fig. 4. EPMA spectrum of a Ta wire exposed to molecular phosphorus for 60 min at 2500 K. No signal could be observed at the wavelength of P Ka, indicated by the arrow.
Fig. 1
Fig. 2
Fig. 3
Fig. 4