



Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Decomposition processes of diborane and borazane (ammonia-borane complex) on hot wire surfaces

Hironobu Umemoto^{a,b,*}, Atsushi Miyata^c

^a Graduate School of Engineering, Shizuoka University, Hamamatsu, Shizuoka 432-8561, Japan

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

^c Faculty of Engineering, Shizuoka University, Hamamatsu, Shizuoka 432-8561, Japan

ARTICLE INFO

Available online xxxx

Keywords:

Catalytic doping

Catalytic decomposition

Hot-wire

Mass spectrometric detection

Diborane

Borazane

ABSTRACT

The decomposition efficiencies of B₂H₆ and H₃NBH₃ activated on hot wire surfaces were measured mass spectrometrically. The decomposition efficiency of B₂H₆ increased with the residence time of gases in the chamber, and decreased with total pressure when He was added. Decomposition efficiency was still high even under collision-free conditions. These results suggest that the decomposition is not thermal but catalytic, at least at low pressures, although the wire-material dependence of the decomposition efficiency was minor. The decomposition efficiency of H₃NBH₃ vapor was higher than that of B₂H₆ and increased with the addition of H₂, NH₃, and N₂ as well as H₂NBH₂ were identified as stable decomposition products. These results indicate H₃NBH₃ is a viable candidate as a safe dopant precursor for B-atom doping.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

B₂H₆ is one of the most widely used dopant materials of B atoms in the semiconductor industry. Recently, Matsumura et al. have shown that B atoms can be doped into crystalline silicon surfaces by decomposing B₂H₆ on heated tungsten wire surfaces [1]. In parallel with their study, one of the present authors has studied the decomposition mechanism of B₂H₆ on heated metal surfaces, showing that B and BH are not produced directly on wire surfaces but are produced through H-atom shifting reactions, BH_x + H → BH_{x-1} + H₂, in the gas phase [2]. This is in contrast to the decomposition processes of PH₃, where P atoms are produced directly on the hot wire surfaces [3]. The primary step of B₂H₆ decomposition should be the production of two BH₃ molecules, which is just 133 kJ mol⁻¹ endothermic according to our Gaussian calculations at the QCISD/6-31+G(d,p) level of theory [2,4]. The question is how BH₃ is produced. It has been shown that B₂H₆ can be decomposed thermally in the gas phase [5–12]. Of course, catalytic decomposition on hot wire surfaces can also be expected [12]. Comerford et al. considered that the former is more important under their rather high-pressure conditions, such as 2.7 kPa, although the contribution of the latter process has also been referenced [13,14]. One technique to distinguish these processes is to examine the wire material dependence of the decomposition efficiencies. It has been demonstrated that the decomposition processes of SiH₄, PH₃, and P₄ are catalytic since wire material dependences have been observed [15–17]. Another technique is

to examine the total pressure dependence of the decomposition efficiencies. The decomposition efficiency must increase with the pressure if the decomposition takes place thermally in the gas phase [18].

In the present study, the decomposition efficiencies of B₂H₆ activated on heated W wires were measured under various pressure conditions. Ta and Mo also were used as wire materials. In addition, the decomposition efficiency of H₃NBH₃ was measured as a function of wire temperature. H₃NBH₃ is a non-explosive solid material and can be decomposed easily. The H₃N–BH₃ bond energy is 98 kJ mol⁻¹ according to our Gaussian calculations [4]. The vapor pressure of H₃NBH₃ is ~0.01 Pa at room temperature. This vapor pressure may be too low for film deposition, but it is high enough for doping. H₃NBH₃ is expected to be one of the safe dopant precursors of B atoms.

2. Experimental details

The experimental procedure and apparatus were similar to those described elsewhere [2,3,16,17,19]. B₂H₆ diluted with He and H₂(D₂) were introduced into a cylindrical chamber evacuated by a turbomolecular pump (Osaka Vacuum, TG220FCAB) through mass flow controllers (Horiba STEC, SEC-40M or SEC-7320M). H₃NBH₃ could be effused into the chamber from its reservoir. A butterfly valve was set between the reservoir and the chamber so that the H₃NBH₃ flow could be shut off. The material gases were decomposed by a coiled wire (30 cm in length and 0.39 mm in diameter), which could be resistively heated with a DC power supply (Takasago, EX-1125H2). The wire temperature was measured with a two-wavelength thermometer (LumaSense Technologies, ISR 12-LO). The H₃NBH₃ reservoir was set at a sidearm of the chamber where the thermal radiation from the hot wire could be shaded. The

* Corresponding author at: Graduate School of Engineering, Shizuoka University, Hamamatsu, Shizuoka 432-8561, Japan. Tel./fax: +81 53 478 1275.

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

reservoir was kept at room temperature. All the wires were heated in the presence of B_2H_6/He at least for an hour for boronization before use.

A quadrupole mass-spectrometer (Anelva, M-QA200TS) was attached to the chamber with or without a sampling hole. The mass-spectrometer was differentially pumped with another turbo molecular pump (Osaka Vacuum, TG350FCWB). When a sampling hole was not installed, as was the case for H_3NBH_3 , a butterfly valve was used to create a pressure gradient. The electron impact energy was 70 eV.

H_2 (Japan Air Gases, 99.999%), D_2 (Sumitomo Seika, isotopic purity 99.5%), B_2H_6 (Takachiho Kako, diluted with He to 2.0%), and He (Japan Air Gases, 99.999%) were used from cylinders without further purification. H_3NBH_3 was obtained from Aldrich and the purity was 98.3%. W (99.95%), Mo (99.95%), and Ta (99.95%) wires were products of Nilaco.

3. Results and discussion

3.1. Mass spectrometric measurements on B_2H_6

Fig. 1 shows typical mass spectra of B_2H_6 obtained under collision-free conditions. In this figure, the background signals such as those for H_2O ejected from chamber walls are subtracted. The mass signals decreased with the wire temperature corresponding to the decomposition of B_2H_6 , but the pattern was independent of the temperature. Similar spectra could be obtained under other conditions. Although the mass signal of $^{11}B_2H_6^+$ at a mass-to-charge ratio (m/z) of 28 was hard to observe, the decomposition efficiency of B_2H_6 can be determined by measuring the mass signal of one of the fragment ions, $^{11}B_2H_2^+$ at $m/z = 24$, which was free from background signals. The decomposition efficiencies thus determined were more than 50% when the wire temperature was over 1500 K under any pressure conditions and the efficiency saturated over 2000 K. Table 1 summarizes the decomposition efficiencies of B_2H_6 at ~ 2100 K. In these measurements, a sampling hole was used except for the last one under collision-free conditions. The residence time was estimated from the flow rate, chamber volume, and the total pressure. The results can be summarized as follows:

- (1) Decomposition efficiency increases with an increase in the residence time. When the residence time was changed from 0.59 s to 1.18 s with keeping the total pressure at 1.9 Pa, the decomposition efficiency increased from 0.72 to 0.88.
- (2) Decomposition efficiency decreases with the total pressure. When the total pressure was changed from 1.9 Pa to 11.4 Pa with keeping the residence time at 0.59 s, the decomposition efficiency decreased from 0.72 to 0.62.
- (3) Decomposition efficiency is still high under collision-free conditions; 0.78.

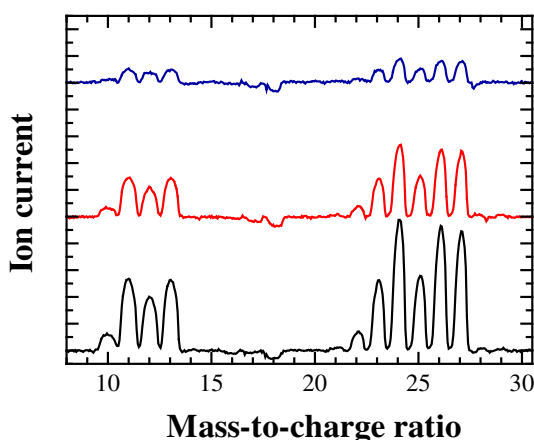


Fig. 1. Mass spectra of B_2H_6 under collision free conditions. W wire temperatures were 2100, 1390, and 300 K from up to bottom.

- (4) The effect of the addition of a small amount of H_2 (D_2) is not remarkable. The decrease in efficiency when H_2 (D_2) was introduced can be explained by the change in residence time.
- (5) The wire material dependence is minor.

The decrease in the decomposition efficiency of B_2H_6 when He was added as well as the high efficiency under collision-free conditions suggest that the decomposition takes place catalytically on the wire surfaces under low-pressure conditions, such as those in the present cases. In general, according to the Lindemann–Hinshelwood mechanism, the rate of a unimolecular decomposition reaction in the gas phase increases with total pressure and then saturates [18]. At low pressures, the collisional energization should be rate-determining and the pseudo-first-order rate constant is expected to increase linearly against total pressure. The decrease in decomposition efficiency with the addition of He can be explained by the presence of termolecular recombination processes to reproduce B_2H_6 , if the rate constant for the recombination is as large as that for $2CH_3 \rightarrow C_2H_6$ [20]. Another possibility is the reduced diffusional transfer of B_2H_6 to wire surfaces at high pressures. The minor effect of the addition of H_2 (D_2) on the decomposition efficiency suggests that the $B_2H_6 + H(D) \rightarrow B_2H_5 + H_2(HD)$ reaction is not important. This reaction is endothermic by 1 kJ mol^{-1} and has a rather high activation barrier, 61 kJ mol^{-1} . The rate constant at moderate temperatures must be small [2]. The reproduction of B_2H_6 from H atoms and deposited B-compounds on chamber walls cannot be expected, either [2]. The decomposition efficiencies showed minor dependence on the wire materials, in contrast to the decomposition of SiH_4 and PH_3 [15,16]. This may be related to the rapid formation of boronized compounds on the wire surfaces.

H_2 could be identified as a stable decomposition product [2], but it was impossible to confirm the production of BH_3 even under collision-free conditions in which a sampling hole was not used. Mass peaks corresponding to BH_x^+ could be identified, but these peaks were ascribed to the fragment ions produced from the parent B_2H_6 . The BH_3 produced may deposit rapidly on chamber walls. In addition, the ionization efficiency of BH_3 may be smaller than that of B_2H_6 in the production of BH_x^+ .

3.2. Mass spectrometric measurements on H_3NBH_3

The decomposition of H_3NBH_3 was confirmed mass spectrometrically. Fig. 2 shows the mass spectra at three W wire temperatures. The background signals are subtracted as for Fig. 1. The parent $H_3NBH_3^+$ ion signal was weak, but it was easy to observe fragment ions, such as $H_3NBH_2^+$, $H_3NBH^+(H_2NBH_2^+)$, and H_2NBH^+ . According to our ab initio calculations at the QCISD/6-31 + G(d,p) level of theory [4], these ions are stable, while some ions such as $H_2NBH_3^+$ are unstable. The decomposition efficiency of H_3NBH_3 at 2230 K, derived from the mass signal of $H_3N^{11}BH_2^+$ at $m/z = 30$, was 86%. Since the total pressure is fairly low under the present conditions, ~ 0.01 Pa, H_3NBH_3 must be decomposed on wire surfaces only.

As shown in Fig. 2, the mass pattern changes with wire temperature. When the wire was not heated, the mass signal at $m/z = 30$ was larger than that at $m/z = 29$. On the other hand, over 1700 K, the peak at $m/z = 29$ was stronger. When the wire is heated, the peak at $m/z = 29$ cannot be ascribed only to the fragment ions produced from H_3NBH_3 , but should contain the contribution of $H_2NBH_2^+$ ions produced from one of the stable products, H_2NBH_2 (boranamine). The production of H_2NBH_2 and H_2 from H_3NBH_3 is 38 kJ mol^{-1} exothermic according to our calculations. H_3NBH and H_3NBH_2 are chemically unstable and their densities should be too small to contribute to the production of H_3NBH^+ or $H_2NBH_2^+$.

It is possible to evaluate the wire temperature dependence of the relative density of H_2NBH_2 . When the wire is not heated, the signal at $m/z = 29$ is solely ascribed to the fragment ions of H_3NBH_3 . We can

Table 1
Decomposition efficiencies of B_2H_6 at ~ 2100 K.

B_2H_6/He flow rate/sccm	H_2 flow rate/sccm	D_2 flow rate/sccm	He flow rate/sccm	Total pressure/Pa	Wire material	Residence time/s	Decomposition efficiency
20	0	0	0	3.3	W	0.51	0.67
10	0	0	0	1.9	W	0.59	0.72
5	0	0	0	1.9	W	1.18	0.88
10	0	0	50	11.4	W	0.59	0.62
10	0	0	20	5.6	W	0.57	0.71
10	0	0	15	3.9	W	0.49	0.67
10	0	15	0	3.9	W	0.49	0.64
10	20	0	0	3.9	W	0.40	0.55
10	0	0	0	1.9	Ta	0.59	0.70
10	0	0	0	1.9	Mo	0.59	0.73
0.38	0	0	0	$\sim 10^{-2a}$	W	$\sim 0.1^a$	0.78

^a The pressure and the residence time for collision-free conditions are rough estimates.

subtract the contribution of these fragment ions, since the fragmentation pattern may not change with wire temperature. The signal intensity at $m/z = 29$ after subtraction should represent the density of H_2NBH_2 .

The mass signal at $m/z = 29$ can be attributed to $[H_2N^{11}BH_2^+]$ from $H_3N^{11}BH_3 (=a)$, $[H_2N^{11}BH_2^+]$ from $H_2N^{11}BH_2 (=b)$, $[H_3N^{11}BH^+]$ from $H_3N^{11}BH_3 (=c)$, and $[H_3N^{10}BH_2^+]$ from $H_3N^{10}BH_3 (=d)$. That at $m/z = 30$ should be $[H_3N^{11}BH_2^+]$ from $H_3N^{11}BH_3 (=e)$ and $[H_3N^{10}BH_3^+]$ from $H_3N^{10}BH_3 (=f)$, while that at $m/z = 31$ should be $[H_3N^{11}BH_3^+]$ from $H_3N^{11}BH_3 (=g)$. Now, since $g \approx 0$, it may be assumed that $f \approx 0$. When the wire is not heated, the ratio of the mass signal at $m/z = 29$ to that at $m/z = 30$ should correspond to $(a + c + d)/e$. From the mass signal ratio when the wire is heated, we obtain the ratio of $a' + b' + c' + d'$ to e' , where primed characters represent the mass signals when the wire is heated. The ratio of $a' + c' + d'$ to e' may be assumed to be the same as that when the wire is not heated, $(a + c + d)/e$. Then, we can determine the ratio of b' to e' , and consequently the ratio of b' to e . For example, from the measurement at room temperature, we obtain $(a + c + d)/e = 0.88$. Measurements at 2230 K show that $(a' + b' + c' + d')/e' = 2.10$ and $e'/e = 0.14$. Then, we obtain $b'/e = 0.17$. The values of b'/e at different temperatures can be obtained similarly. Unfortunately, since the detection sensitivities for H_2NBH_2 and H_3NBH_3 should be different, only the relative values of b'/e can be determined, but it is possible to evaluate the wire temperature dependence of the relative H_2NBH_2 densities. Fig. 3 shows the results thus obtained. The densities were normalized to its maximum value. The relative intensities of the mass peak at $m/z = 30$, which may represent the H_3NBH_3 densities, normalized to its intensity at 300 K are also illustrated.

The mass signals at $m/z = 2$ and 28 increased monotonically with the wire temperature, while at $m/z = 17$ it increased and then decreased at more than 1750 K. The increases at $m/z = 2$ and 28 can easily be explained by the production of H_2 and N_2 . These species may be

produced not only on wire surfaces but also on chamber walls when H- and NH_x -radicals are present. The signal at $m/z = 17$ should be ascribed to NH_3^+ ; the decrease in the NH_3^+ signal over 1750 K can be explained by the catalytic decomposition of NH_3 on wire surfaces to produce H_2 and N_2 [21]. The increase in the signal at $m/z = 28$ may also be caused by the production of $H_2N^{11}BH^+$ from $H_2N^{11}BH_2$. It is hard to determine the population ratio of N_2 to H_2NBH_2 , but the H_2NBH_2 density may be smaller than that of N_2 , since H_2NBH_2 may be further decomposed on wire surfaces while the decomposition of N_2 is minor [22–24]. If we assume that the H_2NBH_2 density is much smaller than that of N_2 , or the production efficiency of H_2NBH^+ from H_2NBH_2 is the same as the ionization efficiency of N_2 , it is possible to evaluate the relative densities of H_2 , NH_3 , and $N_2 + H_2NBH_2$ by a procedure similar to that used to determine the relative densities of H_2NBH_2 . Here, the production of $H_2N^{10}BH_2^+$ from $H_2N^{10}BH_2$ was ignored just for simplicity. The relative detection sensitivities for H_2 , NH_3 , and N_2 were measured separately. The fragmentation patterns of NH_3 and residual H_2O , whose signal could not be subtracted completely, were included in the present evaluation of the NH_3 densities. Fig. 4 shows the relative densities of H_3NBH_3 and its decomposition products, H_2 , NH_3 , and $N_2 + H_2NBH_2$, as a function of W wire temperature. The H_3NBH_3 densities were normalized to its density at 300 K, while others were normalized to the H_2 density at 2230 K.

The decomposition efficiency of H_3NBH_3 increased with the addition of H_2 , as shown in Fig. 3. When 0.13 sccm ($1 \text{ sccm} = 6.9 \times 10^{-7} \text{ mol s}^{-1}$) of a H_2 flow was introduced, the decomposition efficiency at 2230 K increased to 97%. The total pressure was on the order of 0.1 Pa. This increase in decomposition efficiency cannot be ascribed to the change in residence time. If the residence time is changed

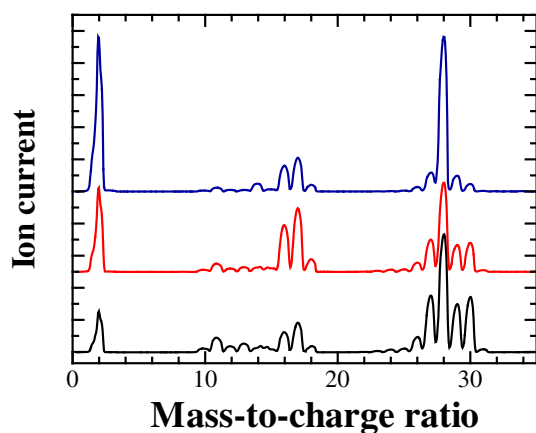


Fig. 2. Mass spectra of H_3NBH_3 and its decomposition products. W wire temperatures were 2230, 1580, and 300 K from up to bottom. No buffer gases were introduced.

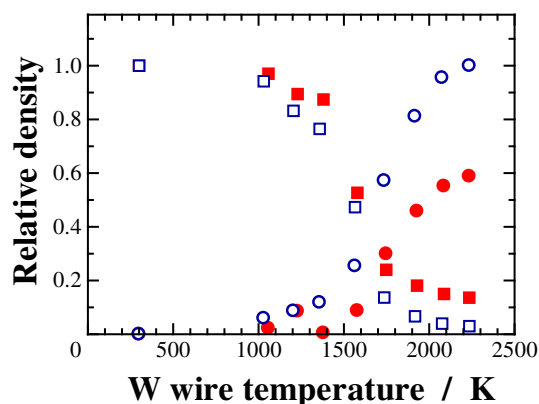


Fig. 3. Relative densities of H_3NBH_3 (■, □) and H_2NBH_2 (●, ○) as a function of W wire temperature. Open symbols represent the results in the presence of a H_2 flow of 0.13 sccm, while closed symbols represent those in its absence. The densities for H_3NBH_3 were normalized to its density at 300 K, while those for H_2NBH_2 were normalized to its density at 2230 K in the presence of a H_2 flow.

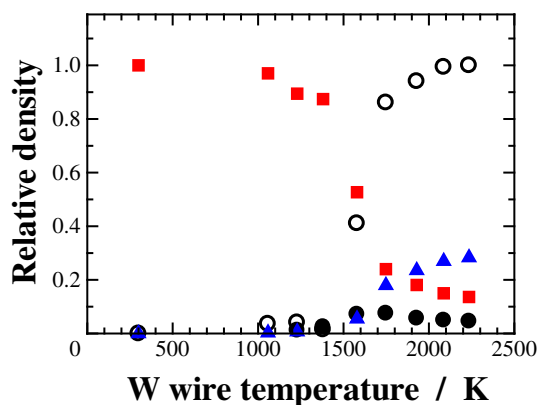


Fig. 4. Relative densities of H_3NBH_3 (■) and its decomposition products, H_2 (○), NH_3 (●), and $\text{N}_2 + \text{H}_2\text{NBH}_2$ (▲), as a function of W wire temperature. No buffer gases were introduced. The densities for H_3NBH_3 were normalized to its density at 300 K, while others were normalized to the H_2 density at 2230 K.

with the introduction of H_2 , it may also be changed with the introduction of He. The decomposition efficiency at 2230 K when 0.13 sccm of a He flow was introduced was 88%, which is only 2% higher than that in the absence of a buffer gas. The increase in decomposition efficiency with the addition of H_2 can be explained by the reaction, $\text{H}_3\text{NBH}_3 + \text{H} \rightarrow \text{H}_3\text{NBH}_2 + \text{H}_2 + 36 \text{ kJ}$, followed by $\text{H} + \text{H}_3\text{NBH}_2 \rightarrow \text{H}_2 + \text{H}_2\text{NBH}_2 + 418 \text{ kJ}$ (or $\text{NH}_3 + \text{BH}_3 + 282 \text{ kJ}$). The exothermicities are the results of ab initio calculations [4]. The above reactions may take place not only on wire surfaces but also in the gas phase, since the system is not collision-free when the total pressure is $\sim 0.1 \text{ Pa}$. The potential barrier for the former reaction in the gas phase is calculated to be 38 kJ mol^{-1} , which should be overcome at moderate temperatures. The barrier for a similar reaction, $\text{H} + \text{H}_3\text{NBH}_3 \rightarrow \text{H}_2 + \text{H}_2\text{NBH}_3 + 9 \text{ kJ}$, is calculated to be 72 kJ mol^{-1} , suggesting that this reaction is less important. We cannot determine the population ratio of $[\text{H}_2\text{NBH}_2]$ at 2230 K to $[\text{H}_3\text{NBH}_3]$ at 300 K because the detection sensitivities are not known. However, it is possible to evaluate the ratio of the ratio. The ratio of $[\text{H}_2\text{NBH}_2]$ to $[\text{H}_3\text{NBH}_3]$ was 1.7 times larger in the presence of a H_2 flow than in its absence. This increase is consistent with the above abstraction model. No such increase could be observed when He was added. The wire temperature dependence of the relative densities of the decomposition products, H_2 , NH_3 , N_2 , and H_2NBH_2 , were also measured in the presence of H_2 and He flows and in both cases the dependences were similar to those measured in the absence. Similar results were obtained when Ta and Mo were used as the wire materials. The decomposition efficiency of H_3NBH_3 for Ta was 89% at 2080 K, while that for Mo was 90% at 2090 K.

4. Conclusions

The total pressure dependence of the decomposition efficiencies of B_2H_6 shows that the decomposition takes place catalytically on hot wire surfaces under low-pressure conditions, such as below 11 Pa. The thermal decomposition in the gas phase has minor contributions. The decomposition efficiency of H_3NBH_3 is higher than that of B_2H_6 . H_2 , NH_3 , N_2 , and H_2NBH_2 were identified as stable decomposition products. H_3NBH_3 is one of the candidates for a safe dopant precursor of B atoms.

The decomposition efficiency of H_3NBH_3 increases with the introduction of H_2 . This can be explained by the exothermic abstractive reactions with H atoms. No such reactions take place for B_2H_6 because of a large potential barrier.

Acknowledgment

This work was partially funded by a Grant-in-Aid for Science Research (No. 26410010) from the Japan Society for the Promotion of Science.

References

- [1] H. Matsumura, T. Hayakawa, T. Ohta, Y. Nakashima, M. Miyamoto, T.C. Thi, K. Koyama, K. Ohdaira, Cat-doping: novel method for phosphorus and boron shallow doping in crystalline silicon at 80°C , *J. Appl. Phys.* 116 (2014) 114502.
- [2] H. Umemoto, T. Kanemitsu, A. Tanaka, Production of B atoms and BH radicals from $\text{B}_2\text{H}_6/\text{He}/\text{H}_2$ mixtures activated on heated W wires, *J. Phys. Chem. A* 118 (2014) 5156.
- [3] H. Umemoto, Y. Nishihara, T. Ishikawa, S. Yamamoto, Catalytic decomposition of PH_3 on heated tungsten wire surfaces, *Jpn. J. Appl. Phys.* 51 (2012) 086501.
- [4] GAUSSIAN 09, revision B.01, M. J. Frisch et al., Gaussian, Inc., Wallingford, CT, 2010.
- [5] B. Sun, M.L. McKee, Computational study of the initial stage of diborane pyrolysis, *Inorg. Chem.* 52 (2013) 5962.
- [6] M.D. Attwood, R. Greatrex, N.N. Greenwood, C.D. Potter, Kinetic studies of reactions of hexaborane(10) with other binary boranes in the gas phase, *J. Organomet. Chem.* 614–615 (2000) 144.
- [7] R. Greatrex, N.N. Greenwood, S.M. Lucas, Identity of the rate-determining step in the gas-phase thermolysis of diborane: a reinvestigation of the deuterium kinetic isotope effect, *J. Am. Chem. Soc.* 111 (1989) 8721.
- [8] H. Fernández, J. Grote, C.M. Previtali, Thermal decomposition of diborane. Part I. The decomposition mechanism at low conversion and temperature and inhibiting effect of accumulated hydrogen, *J. Chem. Soc. Dalton Trans.* (1973) 2090.
- [9] A.J. Owen, The pyrolysis of diborane, *J. Appl. Chem.* 10 (1960) 483.
- [10] R.P. Clarke, R.N. Pease, A preliminary study of the kinetics of pyrolysis of diborane, *J. Am. Chem. Soc.* 73 (1951) 2132.
- [11] J.K. Bragg, L.V. McCarty, F.J. Norton, Kinetics of pyrolysis of diborane, *J. Am. Chem. Soc.* 73 (1951) 2134.
- [12] M. Söderlund, P. Mäki-Arvela, K. Eränen, T. Salmi, R. Rahkola, D.Yu. Murzin, Catalyst deactivation in diborane decomposition, *Catal. Lett.* 105 (2005) 191.
- [13] D.W. Comerford, A. Cheesman, T.P.F. Carpenter, D.M.E. Davies, N.A. Fox, R.S. Sage, J.A. Smith, M.N.R. Ashfold, Y.A. Mankelevich, Experimental and modeling studies of B atom number density distributions in hot filament activated $\text{B}_2\text{H}_6/\text{H}_2$ and $\text{B}_2\text{H}_6/\text{CH}_4/\text{H}_2$ gas mixtures, *J. Phys. Chem. A* 110 (2006) 2868.
- [14] Y.A. Mankelevich, M.N.R. Ashfold, D.W. Comerford, J. Ma, J.C. Richley, Boron doping: B/H/C/O gas-phase chemistry; H atom density dependences on pressure and wire temperature; Puzzles regarding the gas-surface mechanism, *Thin Solid Films* 519 (2011) 4421.
- [15] H.L. Duan, S.F. Bent, The influence of filament material on radical production in hot wire chemical vapor deposition of a-Si:H, *Thin Solid Films* 485 (2005) 126.
- [16] H. Umemoto, Dependence of the catalytic decomposition of PH_3 on wire material, *Thin Solid Films* 575 (2015) 9.
- [17] H. Umemoto, T. Kanemitsu, Y. Kuroda, Catalytic decomposition of phosphorus compounds to produce phosphorus atoms, *Jpn. J. Appl. Phys.* 53 (2014) 05FM02.
- [18] K.A. Holbrook, M.J. Pilling, S.H. Robertson, *Unimolecular Reactions*, 2nd ed. John Wiley & Sons, Chichester, England, 1996.
- [19] H. Umemoto, Y. Nishihara, T. Ishikawa, *In-situ* production of PH_3 from red phosphorus and atomic hydrogen, *Chem. Phys. Lett.* 514 (2011) 26.
- [20] B. Wang, H. Hou, L.M. Yoder, J.T. Muckerman, C. Fockenberg, Experimental and theoretical investigations on the methyl–methyl recombination reaction, *J. Phys. Chem. A* 107 (2003) 11414.
- [21] H. Umemoto, K. Ohara, D. Morita, T. Morimoto, M. Yamawaki, A. Masuda, H. Matsumura, Radical species formed by the catalytic decomposition of NH_3 on heated W surfaces, *Jpn. J. Appl. Phys.* 42 (2003) 5315.
- [22] H. Umemoto, A clean source of ground-state N atoms: decomposition of N_2 on heated tungsten, *Appl. Phys. Express* 3 (2010) 076701.
- [23] H. Umemoto, T. Funae, Y.A. Mankelevich, Activation and decomposition of N_2 on heated tungsten filament surfaces, *J. Phys. Chem. C* 115 (2011) 6748.
- [24] Yu.A. Mankelevich, M.N.R. Ashfold, H. Umemoto, Molecular dissociation and vibrational excitation on a metal hot filament surface, *J. Phys. D* 47 (2014) 025503.