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

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### ABSTRACT

The decomposition efficiencies of B<sub>2</sub>H<sub>6</sub> and H<sub>3</sub>NBH<sub>3</sub> activated on hot wire surfaces were measured mass spectrometrically. The decomposition efficiency of B<sub>2</sub>H<sub>6</sub> 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 H<sub>3</sub>NBH<sub>3</sub> vapor was higher than that of B<sub>2</sub>H<sub>6</sub> and increased with the addition of H<sub>2</sub>, NH<sub>3</sub>, and N<sub>2</sub> as well as H<sub>2</sub>NBH<sub>2</sub> were identified as stable decomposition products. These results indicate H<sub>3</sub>NBH<sub>3</sub> is a viable candidate as a safe dopant precursor for B-atom doping.

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### 1. Introduction

B<sub>2</sub>H<sub>6</sub> 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 B<sub>2</sub>H<sub>6</sub> on heated tungsten wire surfaces [1]. In parallel with their study, one of the present authors has studied the decomposition mechanism of B<sub>2</sub>H<sub>6</sub> 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<sub>x</sub> + H → BH<sub>x-1</sub> + H<sub>2</sub>, in the gas phase [2]. This is in contrast to the decomposition processes of PH<sub>3</sub>, where P atoms are produced directly on the hot wire surfaces [3]. The primary step of B<sub>2</sub>H<sub>6</sub> decomposition should be the production of two BH<sub>3</sub> molecules, which is just 133 kJ mol<sup>-1</sup> endothermic according to our Gaussian calculations at the QCISD/6-31+G(d,p) level of theory [2,4]. The question is how BH<sub>3</sub> is produced. It has been shown that B<sub>2</sub>H<sub>6</sub> 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 SiH<sub>4</sub>, PH<sub>3</sub>, and P<sub>4</sub> 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 B<sub>2</sub>H<sub>6</sub> 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 H<sub>3</sub>NBH<sub>3</sub> was measured as a function of wire temperature. H<sub>3</sub>NBH<sub>3</sub> is a non-explosive solid material and can be decomposed easily. The H<sub>3</sub>N–BH<sub>3</sub> bond energy is 98 kJ mol<sup>-1</sup> according to our Gaussian calculations [4]. The vapor pressure of H<sub>3</sub>NBH<sub>3</sub> is ~0.01 Pa at room temperature. This vapor pressure may be too low for film deposition, but it is high enough for doping. H<sub>3</sub>NBH<sub>3</sub> 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]. B<sub>2</sub>H<sub>6</sub> diluted with He and H<sub>2</sub>(D<sub>2</sub>) 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). H<sub>3</sub>NBH<sub>3</sub> could be effused into the chamber from its reservoir. A butterfly valve was set between the reservoir and the chamber so that the H<sub>3</sub>NBH<sub>3</sub> 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 H<sub>3</sub>NBH<sub>3</sub> reservoir was set at a sidearm of the chamber where the thermal radiation from the hot wire could be shaded. The

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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  $\sim 2100$  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.

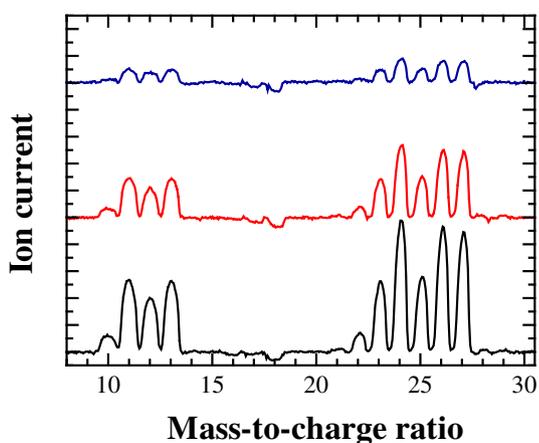


Fig. 1. Mass spectra of  $B_2H_6$  under collision free conditions. W wire temperatures were 2100, 1390, and 300 K from up to bottom.

- (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,  $\sim 0.01$  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<sub>2</sub>H<sub>6</sub> at ~2100 K.

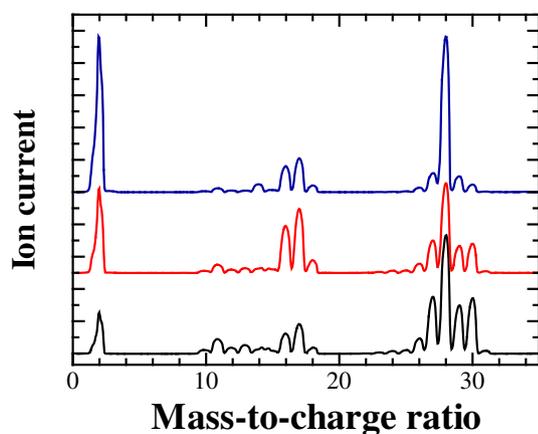
B <sub>2</sub> H <sub>6</sub> /He flow rate/sccm	H <sub>2</sub> flow rate/sccm	D <sub>2</sub> flow rate/sccm	He flow rate/sccm	Total pressure/Pa	Wire material	Residence time/s	Decomposition efficiency
20	0	0	0	3.3	W	0.51	0.67
10	0	0	0	1.9	W	0.59	0.72
5	0	0	0	1.9	W	1.18	0.88
10	0	0	50	11.4	W	0.59	0.62
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	~10 <sup>-2a</sup>	W	~0.1 <sup>a</sup>	0.78

<sup>a</sup> 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<sub>2</sub>NBH<sub>2</sub>.

The mass signal at  $m/z = 29$  can be attributed to [H<sub>2</sub>N<sup>11</sup>BH<sub>2</sub><sup>+</sup>] from H<sub>3</sub>N<sup>11</sup>BH<sub>3</sub> (=a), [H<sub>2</sub>N<sup>11</sup>BH<sub>2</sub><sup>+</sup>] from H<sub>2</sub>N<sup>11</sup>BH<sub>2</sub> (=b), [H<sub>3</sub>N<sup>11</sup>BH<sup>+</sup>] from H<sub>3</sub>N<sup>11</sup>BH<sub>3</sub> (=c), and [H<sub>3</sub>N<sup>10</sup>BH<sub>2</sub><sup>+</sup>] from H<sub>3</sub>N<sup>10</sup>BH<sub>3</sub> (=d). That at  $m/z = 30$  should be [H<sub>3</sub>N<sup>11</sup>BH<sub>2</sub><sup>+</sup>] from H<sub>3</sub>N<sup>11</sup>BH<sub>3</sub> (=e) and [H<sub>3</sub>N<sup>10</sup>BH<sub>3</sub><sup>+</sup>] from H<sub>3</sub>N<sup>10</sup>BH<sub>3</sub> (=f), while that at  $m/z = 31$  should be [H<sub>3</sub>N<sup>11</sup>BH<sub>3</sub><sup>+</sup>] from H<sub>3</sub>N<sup>11</sup>BH<sub>3</sub> (=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  $a' + b' + c' + d'$  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<sub>2</sub>NBH<sub>2</sub> and H<sub>3</sub>NBH<sub>3</sub> 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<sub>2</sub>NBH<sub>2</sub> 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<sub>3</sub>NBH<sub>3</sub> densities, normalized to its intensity at 300 K are also illustrated.

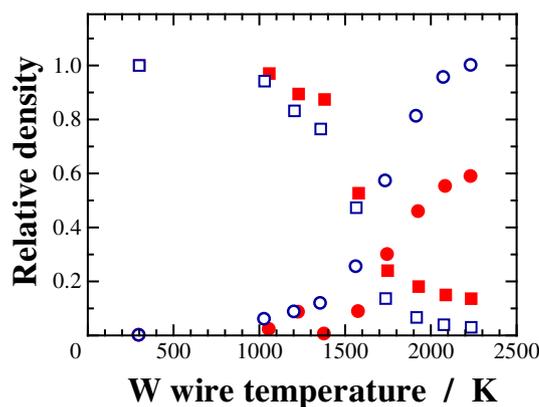
The mass signals at  $m/z = 2$  and 28 increased monotonically with the wire temperature, while at  $m/z = 17$  it increased and then decreased at more than 1750 K. The increases at  $m/z = 2$  and 28 can easily be explained by the production of H<sub>2</sub> and N<sub>2</sub>. These species may be



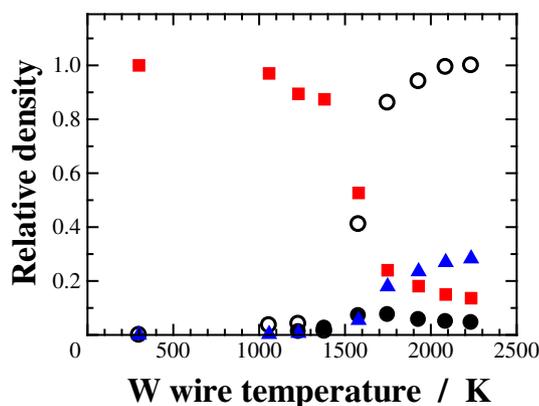
**Fig. 2.** Mass spectra of H<sub>3</sub>NBH<sub>3</sub> and its decomposition products. W wire temperatures were 2230, 1580, and 300 K from up to bottom. No buffer gases were introduced.

produced not only on wire surfaces but also on chamber walls when H- and NH<sub>x</sub>-radicals are present. The signal at  $m/z = 17$  should be ascribed to NH<sub>3</sub><sup>+</sup>; the decrease in the NH<sub>3</sub><sup>+</sup> signal over 1750 K can be explained by the catalytic decomposition of NH<sub>3</sub> on wire surfaces to produce H<sub>2</sub> and N<sub>2</sub> [21]. The increase in the signal at  $m/z = 28$  may also be caused by the production of H<sub>2</sub>N<sup>11</sup>BH<sup>+</sup> from H<sub>2</sub>N<sup>11</sup>BH<sub>2</sub>. It is hard to determine the population ratio of N<sub>2</sub> to H<sub>2</sub>NBH<sub>2</sub>, but the H<sub>2</sub>NBH<sub>2</sub> density may be smaller than that of N<sub>2</sub>, since H<sub>2</sub>NBH<sub>2</sub> may be further decomposed on wire surfaces while the decomposition of N<sub>2</sub> is minor [22–24]. If we assume that the H<sub>2</sub>NBH<sub>2</sub> density is much smaller than that of N<sub>2</sub>, or the production efficiency of H<sub>2</sub>NBH<sup>+</sup> from H<sub>2</sub>NBH<sub>2</sub> is the same as the ionization efficiency of N<sub>2</sub>, it is possible to evaluate the relative densities of H<sub>2</sub>, NH<sub>3</sub>, and N<sub>2</sub> + H<sub>2</sub>NBH<sub>2</sub> by a procedure similar to that used to determine the relative densities of H<sub>2</sub>NBH<sub>2</sub>. Here, the production of H<sub>2</sub>N<sup>10</sup>BH<sub>2</sub><sup>+</sup> from H<sub>2</sub>N<sup>10</sup>BH<sub>2</sub> was ignored just for simplicity. The relative detection sensitivities for H<sub>2</sub>, NH<sub>3</sub>, and N<sub>2</sub> were measured separately. The fragmentation patterns of NH<sub>3</sub> and residual H<sub>2</sub>O, whose signal could not be subtracted completely, were included in the present evaluation of the NH<sub>3</sub> densities. Fig. 4 shows the relative densities of H<sub>3</sub>NBH<sub>3</sub> and its decomposition products, H<sub>2</sub>, NH<sub>3</sub>, and N<sub>2</sub> + H<sub>2</sub>NBH<sub>2</sub>, as a function of W wire temperature. The H<sub>3</sub>NBH<sub>3</sub> densities were normalized to its density at 300 K, while others were normalized to the H<sub>2</sub> density at 2230 K.

The decomposition efficiency of H<sub>3</sub>NBH<sub>3</sub> increased with the addition of H<sub>2</sub>, as shown in Fig. 3. When 0.13 sccm (1 sccm = 6.9 × 10<sup>-7</sup> mol s<sup>-1</sup>) of a H<sub>2</sub> 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. 3.** Relative densities of H<sub>3</sub>NBH<sub>3</sub> (■, □) and H<sub>2</sub>NBH<sub>2</sub> (●, ○) as a function of W wire temperature. Open symbols represent the results in the presence of a H<sub>2</sub> flow of 0.13 sccm, while closed symbols represent those in its absence. The densities for H<sub>3</sub>NBH<sub>3</sub> were normalized to its density at 300 K, while those for H<sub>2</sub>NBH<sub>2</sub> were normalized to its density at 2230 K in the presence of a H<sub>2</sub> flow.



**Fig. 4.** Relative densities of  $\text{H}_3\text{NBH}_3$  (■) and its decomposition products,  $\text{H}_2$  (○),  $\text{NH}_3$  (●), 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  $\text{H}_3\text{NBH}_3$  were normalized to its density at 300 K, while others were normalized to the  $\text{H}_2$  density at 2230 K.

with the introduction of  $\text{H}_2$ , 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  $\text{H}_2$  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  $38 \text{ kJ mol}^{-1}$ , 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  $72 \text{ kJ mol}^{-1}$ , 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  $\text{H}_2$  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,  $\text{H}_2$ ,  $\text{NH}_3$ ,  $\text{N}_2$ , and  $\text{H}_2\text{NBH}_2$ , were also measured in the presence of  $\text{H}_2$  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  $\text{H}_3\text{NBH}_3$  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  $\text{B}_2\text{H}_6$  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  $\text{H}_3\text{NBH}_3$  is higher than that of  $\text{B}_2\text{H}_6$ .  $\text{H}_2$ ,  $\text{NH}_3$ ,  $\text{N}_2$ , and  $\text{H}_2\text{NBH}_2$  were identified as stable decomposition products.  $\text{H}_3\text{NBH}_3$  is one of the candidates for a safe dopant precursor of B atoms.

The decomposition efficiency of  $\text{H}_3\text{NBH}_3$  increases with the introduction of  $\text{H}_2$ . This can be explained by the exothermic abstractive reactions with H atoms. No such reactions take place for  $\text{B}_2\text{H}_6$  because of a large potential barrier.

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