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Decomposition processes of H_3NBH_3 (borazane), $(\text{BH})_3(\text{NH})_3$ (borazine), and $\text{B}(\text{CH}_3)_3$ (trimethylboron) on heated W wire surfaces

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Abstract

The decomposition mechanisms of H_3NBH_3 , $(\text{BH})_3(\text{NH})_3$, and $\text{B}(\text{CH}_3)_3$ on heated W wire surfaces were examined using mass spectrometric and laser spectroscopic techniques. These chemicals can be source materials for catalytic chemical vapor deposition as well as for B-atom doping. All the species could be decomposed well when the wire temperature was over 2.0×10^3 K. When H_2 was introduced, the production of B atoms was confirmed in the decomposition of H_3NBH_3 and $\text{B}(\text{CH}_3)_3$, but not for $(\text{BH})_3(\text{NH})_3$. H_3NBH_3 and $\text{B}(\text{CH}_3)_3$ may be candidates as safe precursors for B-atom doping, while $(\text{BH})_3(\text{NH})_3$ could be a viable candidate as a BN film precursor.

1. Introduction

B-atom doping is an essential technique in the semiconductor industry, and one of the most typical precursors in catalytic doping is B_2H_6 [1,2]. The decomposition mechanism of B_2H_6 activated on heated W wire surfaces has recently been examined by one of the present authors and it has been shown that B and BH are produced efficiently in the presence of an excess amount of H_2 [3]. B_2H_6 must be decomposed to BH_3 on wire surfaces, while B and BH are produced from BH_3 through H-atom shifting reactions, $BH_x + H \rightarrow BH_{x-1} + H_2$, in the gas phase [3,4]. Although B_2H_6 can be a useful dopant material, it is not only toxic, but also explosive. Recently, we have shown that H_3NBH_3 can be decomposed on hot-wire surfaces and that this can be a safe source material for B-atom doping [4]. Mass spectrometric measurements showed that its decomposition efficiency is 86% when the wire temperature is 2.23×10^3 K and the decomposition efficiency increases even more with the addition of H_2 . These efficiencies are higher than those for B_2H_6 , which has an efficiency of around 70% at 2.0×10^3 K and depends little on the wire temperature over this temperature [3,4]. However, since the vapor pressure of H_3NBH_3 , ~ 0.01 Pa at room temperature, is much lower than that of B_2H_6 , it is necessary to ascertain that a high enough amount of active species, such as B atoms, is produced from H_3NBH_3 . $(BH)_3(NH)_3$, which has a benzene-like ring structure, and $B(CH_3)_3$ are other safe candidate sources of B-atoms. The vapor pressures of these materials are much higher than that of H_3NBH_3 , but it is uncertain if the B-N and B-C bonds can be broken on hot wire surfaces. It has been shown that P atoms are produced efficiently from $P(C_2H_5)_3$ on heated metal wire surfaces [5], while the production of Si atoms from $Si(CH_3)_4$ is rather minor [6,7]. $B(OCH_3)_3$ has also been used to prepare boron-doped diamond films [8-10]. It has been reported, however, that W and Ta are less suitable filament materials to decompose $B(OCH_3)_3$, possibly because of the rapid formation of volatile metal oxides [10].

2. Experimental

The experimental procedure and apparatus for this study were similar to those described elsewhere [3,4]. H_3NBH_3 was effused into a cylindrical chamber from its reservoir, since its vapor pressure is low, on the order of 0.01 Pa at room temperature. H_2 and He could be used as carrier gases whose flow rates were controlled with a mass flow controller (Horiba STEC, SEC-40M). A butterfly valve was set between the reservoir and the chamber so that the H_3NBH_3 flow could be shut off. The reservoir could be heated; its temperature was controlled with a thermo-controller (AS ONE, TJA-550). The reservoir temperature was measured with a chromel-alumel thermocouple. $(BH)_3(NH)_3$ and $B(CH_3)_3$ have much higher vapor pressures

and were introduced into the chamber through a mass flow controller (Horiba STEC, SEC-410NC) after having been diluted with He to 2.0%. The vacuum chamber was evacuated with a turbomolecular pump (Osaka Vacuum, TG350FCWB) backed with a dry scroll pump (Ulvac, DIS-251).

The material gases were decomposed on a coiled W wire (30 cm in length and 0.39 mm in diameter, Nilaco), which could be resistively heated with a DC power supply (Takasago, EX-1125H2). The wire was boronized by a B₂H₆/He/H₂ mixture before use to minimize the condition changes during the measurements. The wire temperature was measured with a two-wavelength thermometer (LumaSense Technologies, ISR 12-LO).

A quadrupole mass spectrometer (Anelva, M-QA200TS or M-101QA-TDM) was attached to the chamber. A sampling hole or a butterfly valve was used to separate the main chamber and the spectrometer. The mass spectrometer was differentially pumped with another turbomolecular pump (Osaka Vacuum, TG350FCAB). The electron impact energy was 70 eV.

B-atom densities were evaluated using a laser-induced fluorescence (LIF) technique at 249.77 nm, which corresponds to the 2s²3s²S_{1/2} - 2s²2p²P_{3/2} transition. The distance between the wire and the laser beam detection zone was 9 cm. The light source was a dye laser (Sirah, CBST-LG-24) pumped with a neodymium-doped yttrium aluminum garnet (Nd:YAG) laser (Quanta-Ray, PRO-190). A β-BaB₂O₄ (BBO) crystal doubled the frequency of the output. The induced fluorescence was detected with a photomultiplier tube (Hamamatsu Photonics, R212UH) through a collimating lens and an interference filter. The photomultiplier signals were processed with a digital oscilloscope (LeCroy, HDO4032). Absolute densities were evaluated by comparing the signal intensities with that of a known amount of B atoms obtained in a B₂H₆/He/H₂ system under the following conditions: flow rates of B₂H₆/He and H₂ were 10 and 20 sccm, respectively, total pressure was 3.9 Pa, and W wire temperature was 2.05×10³ K.

H₂ (Japan Air Gases, 99.999%), B₂H₆ (Takachiho Kako, diluted with He to 2.0%), and He (Japan Air Gases, 99.999%) were used from cylinders without further purification. H₃NBH₃ was obtained from Aldrich. (BH)₃(NH)₃ was a product of Gas-Phase Growth Ltd., while B(CH₃)₃ was a product of Tri Chemical Laboratories. (BH)₃(NH)₃ and B(CH₃)₃ were diluted with He to 2.0% before use.

3. Results and Discussion

3.1 Mass spectrometric measurements

The mass spectrometric measurements for H₃NBH₃ have been reported elsewhere [4]. Briefly, the decomposition efficiency in the absence of a H₂ flow at 2.23×10³ K was 86%, which is

higher than that for B_2H_6 (~70%). This efficiency increased to 97% when H_2 was introduced, but no such increase was observed when He was added. This increase in the decomposition efficiency has been explained by the reaction between H atoms and H_3NBH_3 [4]. Besides H_2 , NH_3 , and N_2 , H_2NBH_2 also was identified as a stable product.

As for $(BH)_3(NH)_3$, efficient decomposition was confirmed in both the absence and the presence of a H_2 flow. The decomposition efficiency was derived from the mass signal of $^{11}B_3N_3H_5^+$ at the mass-to-charge ratio (m/z) of 80, since this ion peak was stronger than the parent ion peak at $m/z=81$. The $^{11}B_3N_3H_5^+$ ion should be $^{11}B(^{11}BH)_2(NH)_3^+$ because our ab initio calculations at the QCISD/6-31+G(d,p) level of theory [11] show that this ion is more stable than $(^{11}BH)_3(NH)_2N^+$. In the absence of a H_2 flow, the decomposition efficiency was 96% when the W wire temperature was 2.31×10^3 K. The efficiency decreased to 90% when 10 sccm of a H_2 flow was introduced. Figure 1 shows the decomposition efficiencies, evaluated from the differences in the mass signal at room temperature and those at elevated temperatures, as a function of wire temperature. This figure shows that the decomposition is mass-transport limited over 1.9×10^3 K. The decrease in decomposition efficiency with the introduction of H_2 can be explained by minor reactions between H atoms and $(BH)_3(NH)_3$ as well as the reduction of the residence time of gases. This situation is similar to that observed in the catalytic decomposition of B_2H_6 [3,4]. The residence time may also be shortened in the H_3NBH_3/H_2 systems, but this effect must be minor compared to that caused by the reaction with H atoms. H_2 was the only major stable product observed. It is not certain if a ring opening reaction takes place.

In the mass spectrometric measurements for $B(CH_3)_3$, the signal of the parent ion, $^{11}B(CH_3)_3^+$ at $m/z=56$, as well as those of the $BC_3H_x^+$ ($0 \leq x \leq 8$) ions were too weak to precisely determine the decomposition efficiency, in contrast to the $P(C_2H_5)_3$ systems [5]. On the other hand, $^{11}B(CH_3)_2^+$ at $m/z=41$ could be observed clearly as a fragment ion. The signal at $m/z=41$ decreased when the wire was heated. This decrease at $m/z=41$ suggests the catalytic decomposition of $B(CH_3)_3$. However, since $HB(CH_3)_2$ may be produced as a stable product, only the lower limit of the decomposition efficiency can be determined. $B(CH_3)_2^+$ may be produced from $HB(CH_3)_2$. In order to minimize the effect of secondary processes in the gas phase, the lower limit of the decomposition efficiency was evaluated from the data under collision-free conditions without introducing H_2 , where the total pressure was in the order of 1 mPa. Typical mass spectra under such conditions are shown in Figure 2. The decomposition efficiency at 1.84×10^3 K was determined to be higher than 38%, while at 2.30×10^3 K it is over 45%. The only stable product species observed in the absence of a H_2 flow was H_2 . In the

presence of a H_2 flow of 20 sccm, the production of CH_4 could be confirmed.

3.2 Detection of B atoms in $\text{H}_3\text{NBH}_3/\text{H}_2$ systems

B atoms could be identified in $\text{H}_3\text{NBH}_3/\text{H}_2$ systems. Figure 3 shows the wire temperature dependence of the B-atom densities for $\text{B}_2\text{H}_6/\text{He}/\text{H}_2$, $\text{H}_3\text{NBH}_3/\text{H}_2$, pure H_2 , and $\text{B}(\text{CH}_3)_3/\text{He}/\text{H}_2$ systems. The results for $\text{B}(\text{CH}_3)_3/\text{He}/\text{H}_2$ will be discussed in section 3.4. As has been previously reported, weak B-atom signals can be observed even in the absence of B_2H_6 when boronized W wires are heated [3]. Similar results were reported by Comerford et al. for Ta and Re wires [12]. In Ref. [3], we plotted the differences in B-atom densities measured in the presence and in the absence of a $\text{B}_2\text{H}_6/\text{He}$ flow. In Figure 3, B-atom densities, including those ejected from boronized wire surfaces, are plotted. When the H_3NBH_3 reservoir was heated to 350 K in the presence of a H_2 flow, the B-atom density was comparable to that observed in the $\text{B}_2\text{H}_6/\text{He}/\text{H}_2$ system. The Arrhenius plot for H_3NBH_3 when the reservoir was heated is similar to that for B_2H_6 and shows saturation at high temperatures. This saturation may be ascribed to the near-complete decomposition of H_3NBH_3 on wire surfaces. When the reservoir was not heated, the B-atom signals were weak and comparable to those in the absence of H_3NBH_3 , especially when the wire temperature was high. The minor production of B atoms when the reservoir was not heated can be ascribed to the low vapor pressure of H_3NBH_3 at room temperature.

The B-atom density in $\text{H}_3\text{NBH}_3/\text{He}$ systems was one order of magnitude smaller than the density in $\text{H}_3\text{NBH}_3/\text{H}_2$ systems even when the total pressure was kept the same, regardless of reservoir temperature. This situation is similar to that for B_2H_6 systems and shows that the direct production of B atoms on wire surfaces is minor. We may conclude that H_2 molecules, or more probably H atoms produced from H_2 , play a key role in the production of B atoms. In the decomposition of B_2H_6 , we have posited that the initial step is the production of BH_3 , which is converted step by step to B in H-atom shifting reactions [3]. In the decomposition of H_3NBH_3 , the direct products on wire surfaces must be NH_3 and BH_3 , the latter of which should be converted to B atoms in H-atom shifting reactions. According to our ab initio calculations at the QCISD/6-31+G(d,p) level of theory [11], the N-B bond energy in H_3NBH_3 is 98 kJ mol^{-1} , which is smaller than the endothermicity for the $\text{B}_2\text{H}_6 \rightarrow 2\text{BH}_3$ reaction, 133 kJ mol^{-1} . In addition to the decomposition to NH_3 and BH_3 , H_3NBH_3 may react with H atoms to produce H_2NBH_2 [4]. The production of H_2NBH_2 has been confirmed mass spectrometrically and it has been shown that the production of H_2NBH_2 is enhanced by the addition of H_2 . According to our calculations, the potential barrier for the $\text{H}_3\text{NBH}_3 + \text{H} \rightarrow \text{H}_3\text{NBH}_2 + \text{H}_2$ reaction is 38 kJ

mol⁻¹. This barrier is higher than that for $\text{BH}_3 + \text{H} \rightarrow \text{BH}_2 + \text{H}_2$, 26 kJ mol⁻¹, but much lower than that for $\text{B}_2\text{H}_6 + \text{H} \rightarrow \text{B}_2\text{H}_5 + \text{H}_2$, 60 kJ mol⁻¹, and may be overcome at moderate temperatures. H_3NBH_2 thus produced may further react with H atoms to produce H_2NBH_2 . However, the production of B atoms through H_2NBH_2 is questionable. The production of NH_2 and BH_2 from H_2NBH_2 is 553 kJ mol⁻¹ endothermic. The production of $\text{NH}_3 + \text{BH}$ is less endothermic but the endothermicity is still 457 kJ mol⁻¹. The production of NH and BH_3 is not only more endothermic but also spin-forbidden. The production of BH_x from H_2NBH_2 is less likely, although that cannot completely be excluded.

3.3 Detection of B atoms in $(\text{BH})_3(\text{NH})_3$ systems

The production of B atoms from $(\text{BH})_3(\text{NH})_3$ was inefficient. It was possible to detect B atoms when a wire was heated in the presence of $(\text{BH})_3(\text{NH})_3/\text{He}/\text{H}_2$. However, the density was almost the same as that in a He/H_2 system with the same total pressure when a boronized W wire was used. Although the vapor pressure of $(\text{BH})_3(\text{NH})_3$, 35 kPa at 298 K, is much higher than that of H_3NBH_3 , the B-N bond cleavage to produce BH_x may not take place because of high endothermicities. For example, the fission process to produce two triplet diradicals, $\text{HNBH}\cdot\text{NH}$ and $\cdot\text{HBNHBH}$, is 1149 kJ mol⁻¹ endothermic. The production of $\text{BH}(\text{X } ^1\Sigma^+)$ and ring-typed $(\text{BH})_2(\text{NH})_3$ (1,2,3,4,5-triazadiboroludine) is 736 kJ mol⁻¹ endothermic, while the endothermicity for the production of $\text{BH}(\text{a } ^3\Pi)$ and a triplet-state $(\text{BH})_2(\text{NH})_3$ diradical is still larger, 1158 kJ mol⁻¹. In addition, these processes may have high activation barriers because two bonds must be broken at a time. On the other hand, the following B-H (N-H) bond cleavage processes are one-step and have moderate endothermicities: $(\text{BH})_3(\text{NH})_3 \rightarrow \text{B}(\text{BH})_2(\text{NH})_3 + \text{H}$ -431 kJ and $(\text{BH})_3(\text{NH})_3 \rightarrow (\text{BH})_3(\text{NH})_2\text{N} + \text{H}$ -472 kJ. The efficient production of H_2 supports the H-atom elimination processes on wire surfaces. Since the decomposition efficiency is high, $(\text{BH})_3(\text{NH})_3$ may be used as a BN-film precursor in catalytic chemical vapor deposition processes.

3.4 Detection of B atoms in $\text{B}(\text{CH}_3)_3/\text{H}_2$ systems

It was easy to detect B atoms in $\text{B}(\text{CH}_3)_3/\text{He}/\text{H}_2$ systems. The B-atom signals were one order more intense compared to those in He/H_2 systems. The results are included in Figure 3. The production efficiency of B atoms from $\text{B}(\text{CH}_3)_3$ is around the same as that from B_2H_6 . The density measurements were carried out at more than 2.05×10^3 K, because the wire temperature was unstable below this temperature, possibly due to the rapid carburization. B-atom density increased monotonously with increases in the flow rates of H_2 and $\text{B}(\text{CH}_3)_3/\text{He}$. This is similar

to the results observed in $B_2H_6/He/H_2$ systems. The minor production of B atoms in the absence of a H_2 flow suggests that the direct product is $B(CH_3)_2$ or BCH_3 , from which B atoms are formed in the following exothermic addition-elimination processes: $H+B(CH_3)_2 \rightarrow HB(CH_3)_2 \rightarrow BCH_3+CH_4+135\text{ kJ}$ and $H+BCH_3 \rightarrow HBCH_3 \rightarrow B+CH_4+67\text{ kJ}$, which are similar to those for $H+BH_x \rightarrow HBH_x \rightarrow BH_{x-1}+H_2$ reactions [3,13,14]. The CH_4 signals observed in the mass spectrometric measurements in the presence of a H_2 flow are consistent with the presence of these processes. The absence of the direct production of B atoms is in contrast to the results in $P(C_2H_5)_3$ systems, in which P atoms are formed directly on wire surfaces, as for the catalytic decomposition of PH_3 [5,15]. This difference may be ascribed to a difference in bond energies. The $(CH_3)_2B-CH_3$ bond energy is 399 kJ mol^{-1} , which is much larger than that of $(C_2H_5)_2P-CH_2CH_3$, which is 242 kJ mol^{-1} [5].

4. Conclusions

H_3NBH_3 , $(BH)_3(NH)_3$, and $B(CH_3)_3$ can be decomposed efficiently on heated W wire surfaces. With H_3NBH_3 and $B(CH_3)_3$, B atoms could be identified in the presence of a H_2 flow. H_3NBH_3 should be decomposed to BH_3 and NH_3 on hot wire surfaces, while B-C bond cleavage must take place for $B(CH_3)_3$. B atoms must be produced in secondary reaction processes with H atoms. These species are candidates for safe precursors for B-atom doping. The absence of the direct production of B atoms from $B(CH_3)_3$ is in contrast to the efficient direct production of P atoms from $P(C_2H_5)_3$, and can be explained by the difference in bond energies. The production of B atoms could not be confirmed in the $(BH)_3(NH)_3/He/H_2$ systems. It must be difficult to break the B-N bonds on hot wire surfaces. The efficient decomposition of $(BH)_3(NH)_3$ without the production of BH_x suggests that $(BH)_3(NH)_3$ might be used to prepare BN films.

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Figure Captions

Figure 1. Decomposition efficiencies of $(\text{BH})_3(\text{NH})_3$ as a function of W wire temperature in the absence (open circle) and in the presence (closed circle) of a H_2 flow of 10 sccm. The $(\text{BH})_3(\text{NH})_3/\text{He}$ flow rates were both 10 sccm, while the total pressures were 1.7 and 2.9 Pa, respectively.

Figure 2. Mass spectra of $\text{B}(\text{CH}_3)_3/\text{He}$ and its decomposed products obtained under collision-free conditions. W wire temperatures were 0.30×10^3 K (upper) and 1.84×10^3 K (lower). Background signals, such as those for H_2O ejected from chamber walls, were subtracted in this figure.

Figure 3. B-atom densities as a function of the reciprocal of the boronized W wire temperature in the presence of a H_2 flow of 20 sccm. Closed squares represent the results in the $\text{B}_2\text{H}_6/\text{He}/\text{H}_2$ system. The $\text{B}_2\text{H}_6/\text{He}$ flow rate was 10 sccm. Open squares represent the results in the $\text{B}(\text{CH}_3)_3/\text{He}/\text{H}_2$ system. The $\text{B}(\text{CH}_3)_3/\text{He}$ flow rate was 10 sccm. Closed triangles and circles represent the results for $\text{H}_3\text{NBH}_3/\text{H}_2$ systems. The H_3NBH_3 reservoir temperatures were 350 K (closed triangle) and 295 K (closed circle), respectively. Open circles represent the results in a pure H_2 system. The total pressure for the $\text{B}_2\text{H}_6/\text{He}/\text{H}_2$ and $\text{B}(\text{CH}_3)_3/\text{He}/\text{H}_2$ systems was 3.9 Pa, while that for $\text{H}_3\text{NBH}_3/\text{H}_2$ and pure H_2 systems was 2.1 Pa.

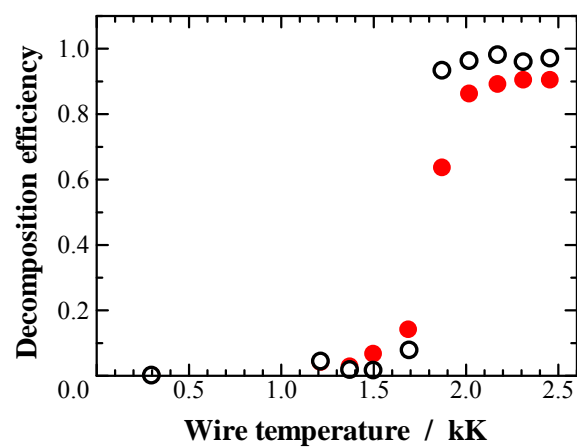


Fig. 1

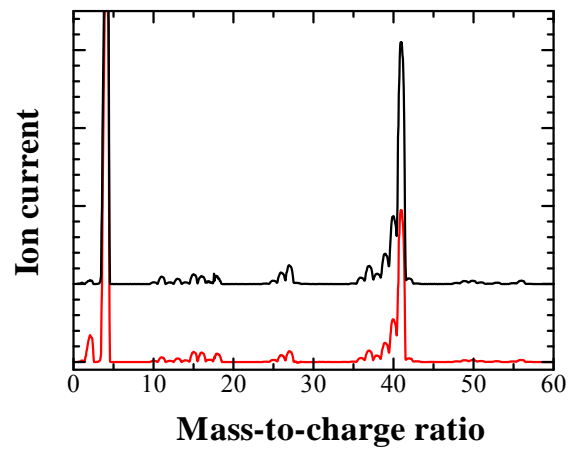


Fig. 2

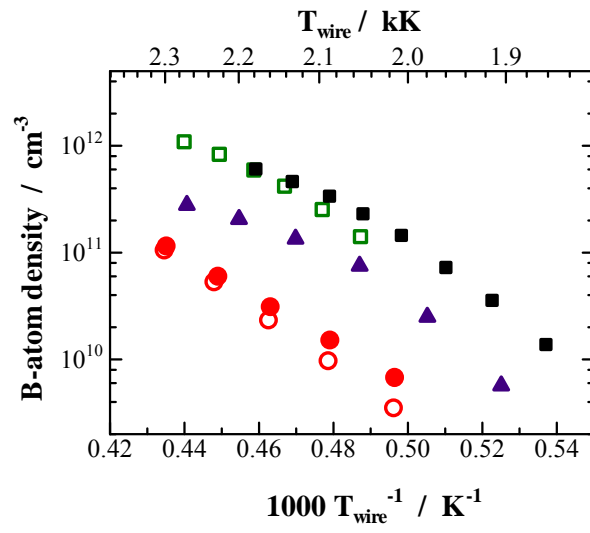


Fig. 3