Hot metal wires as sinks and sources of B atoms

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Abstract

Metal wires, such as W, Mo, and Ta, can be boronized to become sinks of B atoms by heating them in the presence of a mixture of H₂ and H₃NBH₃ or (BH)₃(NH)₃. These boronized wires behave as sources of B atoms when heated in vacuum. The density of B atoms released to the gas phase increases with the addition of H₂ and can be more than 10¹¹ cm⁻³, which is enough for surface doping. The release is stable and continues for more than several hours when boronized for 1 h. Since the metal wires are not nitrated, contamination by N atoms is not expected. H₃NBH₃ and (BH)₃(NH)₃ are not explosive, and wires boronized by these species can be used as safe and contamination-free sources of B atoms for surface doping.

Keywords: hot-wire; boron atoms; borazane; borazine; surface doping

1. Introduction

In hot-wire technologies, material gases are decomposed on heated wire surfaces to produce radical species, which play key roles not only in deposition but also in etching, surface modification, and doping. One of the largest problems in this technology is aging of the wires through the accommodation of material elements. In general, accommodation causes metal wires to become more brittle and catalytically less active. W, one of the most widely used wire materials, can easily be carburized when exposed to organic material gases [1-5]. Silicidation is a problem when we use SiH₄ or organosilicon compounds, although the silicidation by SiH₄ is rather minor at high temperatures, i.e., over 1.8×10^3 K [3-11]. Metal contamination is another problem. W wires can easily be oxidized by O₂ to produce WO_{3-x}, which has much higher vapor pressure than tungsten metal [12].

On the other hand, there have been several reports on utilizing such chemical reactions of filament materials. For example, Schropp and coworkers took advantage of the oxidation of W and succeeded in fabricating amorphous as well as nanostructured tungsten oxide films [13,14]. Carburization of the wire surfaces is also effective for suppressing Si accommodation [9]. The accommodation of B atoms has also been a problem [15,16], but this provides a new technique for doping without using explosive boron compounds [17].

Doping of B atoms can be accomplished without contamination by decomposing B₂H₆ on hot W wire surfaces [18-20]. The problem is that B₂H₆ is not only toxic, but also explosive. Recently, we have shown that borazane (H₃NBH₃), which is not explosive, can be decomposed well on hot-wire surfaces and that B atoms are produced when decomposed in the presence of H₂ [21]. We have also reported that

an efficient and [sustained release](#) of B atoms can be achieved when W wires boronized by $\text{H}_3\text{NBH}_3/\text{H}_2$ were heated in the presence of H_2 , even after the termination of the H_3NBH_3 supply [17]. Since W wires are hardly nitrided, the release of NH_x species, and consequently contamination by N atoms, is not expected. The B-atom density in the gas phase can be [increased to](#) more than 10^{11} cm^{-3} , which is sufficient for surface doping.

In the present study, we extend our previous study and discuss the boronization as well as the release mechanisms on the basis of H_2 flow rate and wire temperature dependences. Not only W, but also Mo and Ta were examined. $(\text{BH})_3(\text{NH})_3$, borazine, which has been proposed as a source material of BN films in hot wire deposition [22], was also tried as a boronizer. The roles of H_2 in both the B-atom production processes and the boronization processes are examined as well. It is shown that B atoms can be released in sufficient quantity for surface doping even in the absence of H atoms, the efficient etchant of Si substrates [23,24].

2. Experimental Details

The experimental procedure and apparatus for this study were similar to those described elsewhere [16,17,21,25]. H_3NBH_3 was effused into a cylindrical chamber from its reservoir. H_2 or He could be used as a carrier gas, with its flow rate controlled by 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. B_2H_6 and $(\text{BH})_3(\text{NH})_3$ were introduced into the chamber after having been diluted with He to 2.0%.

Coiled wires (30 cm in length and 0.39 or 0.40 mm in diameter, Nilaco) were

boronized by exposure to a mixture of H_2 and one of the boron compounds, H_3NBH_3 , $(BH)_3(NH)_3$, or B_2H_6 . The wires were resistively heated with a DC power supply (Takasago, EX-1125H2) up to 2.29×10^3 K. The wire temperature was measured with a two-wavelength thermometer (LumaSense Technologies, ISR 12-LO). B-atom densities in the gas phase were measured both during and after the termination of the boron-compound supply, using a laser-induced fluorescence technique at 249.77 nm, which corresponds to the $2s^23s^2S_{1/2} - 2s^22p^2P_{3/2}$ transition. The distance between the wire and the laser beam detection zone was 9 cm. The light source was a dye laser (Sirah, CSTR-LG-18) pumped with a neodymium-doped yttrium aluminum garnet (Nd:YAG) laser (Quanta-Ray, PRO-170). 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 boxcar averager-gated integrator system (Stanford Research Systems, SR240/SR250/SR280) or a digital oscilloscope (LeCroy, HDO4032). The sources and purities of the gases were the same as those reported elsewhere [17,21].

3. Results and Discussion

[3.1 Wire aging judged from the electric power consumed](#)

During boronization, [as is shown in Fig. 1](#), the electric power needed to keep the wire temperature constant increased at first. After 1 min, the power saturated, while the B-atom density still continued to increase. This shows that the emissivity of the wire surfaces is increased by the boronization of the wire surfaces, while the accommodation and release of B atoms take place simultaneously to reach an equilibrium state. [Fig. 1](#)

[also shows the time dependence of the electric power required to keep the wire temperature constant when 20 sccm \(\$1 \text{ sccm} = 6.9 \times 10^{-7} \text{ mol s}^{-1}\$ \) of \$\text{NH}_3\$ was flown. There was no change at all](#), showing that the nitridation of W is extremely minor.

3.2 Boron source dependence of the B-atom density

[Fig. 2](#) illustrates the time dependence of B-atom densities in the gas phase in the presence of a H_2 flow of 20 sccm, measured after boronizing W wires by $\text{H}_3\text{NBH}_3/\text{H}_2$, $(\text{BH})_3(\text{NH})_3/\text{He}/\text{H}_2$, or $\text{B}_2\text{H}_6/\text{He}/\text{H}_2$. The stable release can be observed for all boronizers and the boron source dependence is minor. It has been confirmed that such release continues for more than 4 h when boronized by $\text{H}_3\text{NBH}_3/\text{H}_2$ [17]. In these measurements, virgin W wires were boronized for 60 min with 2.1 Pa of H_2 . The H_2 pressure during the B-atom density measurement was also 2.1 Pa. The partial pressure of H_3NBH_3 was ~ 0.01 Pa, while those of $(\text{BH})_3(\text{NH})_3$ and B_2H_6 were 0.026 Pa. The wire temperature was kept at 2.29×10^3 K during both the boronization and the B-atom density measurement. Absolute densities, evaluated by comparing the signal intensities with that obtained in the presence of $\text{B}_2\text{H}_6/\text{He}$ and H_2 , were a little different, but these differences should not be overstressed since uncertainty by a factor two cannot be avoided in the absolute density evaluation. No B atoms could be detected when a virgin wire was heated in the presence of H_2 , showing that the production of B atoms from H atoms and boron compounds deposited on chamber walls is minor.

Boronization with He, without a H_2 flow, was also tried, but that was much less efficient for all boron sources. H_2 must play a key role, not only in the production processes of B atoms, as discussed in section [3.4](#), but also in the boronization processes.

3.3 Wire material dependence of the B-atom density

[Fig. 3](#) shows the wire material dependence after boronization by $\text{H}_3\text{NBH}_3/\text{H}_2$. The relative B-atom densities for W, Mo, and Ta are plotted against time. In this figure, the relative values, [normalized by the density just after the end of the boronization](#), are plotted for clarity, since the differences in absolute densities were minor. The decay is the slowest for W and the fastest for Mo, and depended little on the boron sources. In other words, W is the best for a sink and a source. The decay time for Ta evaluated from the plots in [Fig. 3](#) is 3.6×10^2 min. This may seem to contradict the results of Comerford et al., who reported decay times as short as 23 s after switching off the B_2H_6 flow [15]. It should be noted that what they measured must be the evacuation time of B_2H_6 . We could also observe such rapid decays just after the termination of the flow of boron-source gases. We measured the time profile after the initial fast decay. In addition, the partial pressure of B_2H_6 they employed, 1.3 Pa, was much higher than that in the present work. The B-atom density in their measurement must have been much higher than that observed in the present study and the contribution of released B atoms from wire surfaces must have been less remarkable. As for Mo, the deviation from the exponential decay was large and the lifetime was just estimated to be $\sim 1 \times 10^2$ min.

3.4 H_2 flow rate dependence of the B-atom density

When W wires boronized by $\text{H}_3\text{NBH}_3/\text{H}_2$ were heated, B-atom density increased with an increase in the H_2 flow rate [17]. Similar dependences were observed when wires boronized by $(\text{BH})_3(\text{NH})_3/\text{He}/\text{H}_2$ or $\text{B}_2\text{H}_6/\text{He}/\text{H}_2$ were used. The density in the absence of H_2 was 1/5 of that in the presence of a H_2 flow of 20 sccm. It should be noted that this density in pure He systems without H_2 , $4 \times 10^{10} \text{ cm}^{-3}$ at $2.29 \times 10^3 \text{ K}$, is still enough

for surface doping. In other words, it is possible to dope B atoms without exposing H atoms, the efficient etchant of Si substrates [23,24]. One simple explanation for this H_2 flow rate dependence is that BH_x ($1 \leq x \leq 3$) species are mainly released from boronized wires and BH_x species are converted to B atoms by reactions with H atoms formed from H_2 in the gas phase [16]. Another possible role of H atoms in the production of B atoms will be discussed in section 3.5. Similar H_2 flow rate dependences were observed for Mo and Ta, although quantitative measurement was hard for Mo because of its rapid decay. In Ta, the B-atom signal in pure He was much weaker than that in W, showing that the direct ejection of B atoms is minor.

3.5 Wire temperature dependence of the B-atom density

In Fig. 4, B-atom densities are plotted against the reciprocal of the wire temperature for W and Ta. The Arrhenius plot is almost linear for W, while that for Ta shows a little saturation at high temperatures. For W, the activation energy evaluated from the slope in the absence of a H_2 flow, $678 \pm 14 \text{ kJ mol}^{-1}$, is larger than that in its presence, $367 \pm 6 \text{ kJ mol}^{-1}$. The activation energy in the absence of a H_2 flow should represent the energy required to release B atoms directly and is consistent with the calculated adsorption energy of B atoms reported recently, $7 \times 10^2 \text{ kJ mol}^{-1}$ [26]. The weak signals when Ta was used in the absence of a H_2 flow suggest that the Ta-B bond energy is larger than that for W-B. The apparent activation energy in the presence of a H_2 flow should include the contributions of the activation energies to both release BH_x ($1 \leq x \leq 3$) from wire surfaces and produce H atoms from H_2 , $2.4 \times 10^2 \text{ kJ mol}^{-1}$ for W [27]. The apparent activation energy may not be a simple sum of these energies, but the energy required to release BH_x can be estimated to be on the order of $1 \times 10^2 \text{ kJ mol}^{-1}$ for W,

much less than that needed to release B atoms. The small amount of energy required to release BH_x suggests that non-radical species, such as BH_3 , are mainly released. H atoms on wire surfaces may enhance the production and the release of BH_3 .

3.6 Comparison with other systems

It is informative to compare the release processes of B atoms and BH_x species from W to the ejection of other species. Winters et al. have reported that C atoms are released when carburized W is heated [1]. Since the addition of H_2 (D_2) had no effect on the released C-atom densities, they concluded that the release is simple evaporation. The apparent activation energy they observed, $7 \times 10^2 \text{ kJ mol}^{-1}$, should represent the W-C bond energy. This activation energy is similar to that for the release of B atoms and is consistent with the calculated adsorption energy of C atoms on W surfaces, $8 \times 10^2 \text{ kJ mol}^{-1}$, reported recently [28]. Si-atom desorption has also been observed from W wires exposed to SiH_4 [6]. Holt et al. heated silicided W under high vacuum and observed Si atoms mass spectrometrically. The SiH_x ($1 \leq x \leq 4$) signals were very weak under their conditions. Si atoms must be released by simply breaking W-Si bonds. Tong et al., on the other hand, have shown that SiH_4 , SiCH_x ($2 \leq x \leq 5$), and SiC_2H_x ($4 \leq x \leq 7$) are ejected when W wires treated with silacyclobutane are heated in the presence of pure H_2 [7]. It should be noted that they checked the recovery of the aged wires after H_2 etching, excluding the possible formation of SiH_4 and other species from H atoms and silicon/carbon compounds deposited on chamber walls. Since no such species could be observed in the absence of H_2 , chemical processes on the wire surfaces must play key roles in the production of SiH_4 , SiCH_x , and SiC_2H_x . These processes must be similar in the release of BH_x .

4. Conclusions

A novel technique for surface doping of B atoms without the use of explosive boron compounds is presented. In this technique, metal wires are used as sinks and sources of B atoms. B atoms are released by heating metal wires boronized by a mixture of H_2 and H_3NBH_3 or $(BH)_3(NH)_3$. The B-atom density in the gas phase was on the order of 10^{11} cm^{-3} , which is enough for surface doping. N-atom contamination can be avoided by placing substrates after the boronization process, since the metal wires are not nitrified. In addition to W, Mo and Ta also can be used as sinks and sources, but the release was the most stable with W and continued more than several hours after the wires were boronized for 1 h. B-atom density increased with the partial pressure of H_2 , but the density in pure He systems was still 1/5 of that in the presence of a H_2 flow of 20 sccm for W. It is possible to dope B atoms to Si substrates without etching by H atoms under such conditions. [This technique may further be used for deposition, if exposure for a long time is allowed.](#)

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Figure Captions

Fig. 1. Time dependence of the electric power needed to keep the wire temperature constant at 2.29×10^3 K in the presence of $\text{H}_3\text{NBH}_3/\text{H}_2$ (open circle) and NH_3 (closed triangle). The pressure in the $\text{H}_3\text{NBH}_3/\text{H}_2$ system was 2.1 Pa, while that in the NH_3 system was 3.3 Pa when the wire was not heated.

Fig. 2. Time dependence of B-atom densities in the gas phase in the presence of a H_2 flow of 20 sccm, measured after W wires were boronized by $\text{H}_3\text{NBH}_3/\text{H}_2$ (closed circle), $(\text{BH})_3(\text{NH})_3/\text{H}_2$ (closed triangle), or $\text{B}_2\text{H}_6/\text{H}_2$ (closed square). Boronization was carried out for 60 min with 2.1 Pa of H_2 , while the B-atom densities were measured in the presence of 2.1 Pa of H_2 . The W wire temperature was kept at 2.29×10^3 K during both the boronization and the B-atom density measurement.

Fig. 3. Time dependence of relative B-atom densities in the gas phase in the presence of a H_2 flow of 20 sccm measured after the boronization of W (closed circle), Mo (open circle), and Ta (open square) wires. Boronization was carried out for 60 min in the presence of ~ 0.01 Pa of H_3NBH_3 and 2.1 Pa of H_2 , while the B-atom densities were measured in the presence of 2.1 Pa of H_2 . The wire temperature was kept at 2.29×10^3 K during both the boronization and the B-atom density measurement.

Fig. 4. B-atom densities in the gas phase as a function of the reciprocal of boronized wire temperature. Closed circles represent the results for W measured in the presence of 2.1 Pa of H_2 . Open squares represent the results for Ta measured in the presence of

2.1 Pa of H₂. Open circles represent the results for W measured in the presence of 2.1 Pa of He. [The solid lines are the least-squares fit.](#)

Figures 1

Figures 2

Figures 3

Figures 4