A Clean Source of B atoms without Using Explosive Boron Compounds

A Clean Source of B atoms without Using Explosive Boron Compounds

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Efficient sustained-release of B atoms, sufficient for doping to semiconductor substrates, was achieved when W wires boronized by NH_3BH_3/H_2 were heated in the presence of H_2.   The B-atom density in the gas phase was on the order of 10^{11} cm^{-3} and could be kept constant more than 240 min.

Matsumura and coworkers have shown that surface doping of B atoms can be carried out by exposing crystalline Si to the active species formed by the catalytic cracking of B_2H_6 on hot W wire surfaces.[1,2]   Such surface doping makes it possible to control the surface potential of crystalline Si, and consequently to reduce the surface recombination velocity of minority carriers.   The problem is that B_2H_6 is not only toxic, but also explosive.   Recently, we have reported that NH_3BH_3,

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borazane, can be decomposed efficiently on hot-wire surfaces and that this can be a safer source material for B-atom doping.[3,4] NH_3BH_3 is decomposed to NH_3 and BH_3, while BH_3 can be converted to B atoms in gas-phase reactions with H atoms.   H atoms can easily be produced from H_2 on heated wire surfaces.[5,6]   Although the vapor pressure of NH_3BH_3 is low, around 0.01 Pa at room temperature, the B-atom density produced from NH_3BH_3 can be increased up to 3×10^{11} cm^{-3} by heating the NH_3BH_3 reservoir to 350 K.   This density is comparable to that produced by the catalytic decomposition of B_2H_6/H_2,[4,7] and sufficient for doping to semiconductor substrates.   One problem with this boron-nitrogen-hydrogen compound is the possible contamination by N atoms. N_2 is fairly stable,[8] but NH_3 can easily be decomposed to NH_2 and H on hot wire surfaces.[9]   The incorporation of N atoms cannot completely be avoided.[10]

Comerford et al. have reported that Ta wires can be boronized when heated in the presence of B_2H_6/H_2 and that B atoms can be observed even after the B_2H_6 supply has been terminated.[11]   We also found that W wires can be boronized by B_2H_6/H_2 and that B atoms are released from the boronized wires when heated in the presence of a H_2 flow.[7]   In the case of Ta wires, the B-atom density decays rather rapidly, within 1 min, after switching off the B_2H_6 flow, but the decay time for W wires was found to be much longer.[7,11]   In the present study, we report that W wires also can be boronized when exposed to NH_3BH_3/H_2 and that B atoms can be supplied stably from these boronized wires.   Similar measurements with W wires boronized by $B_2H_6/He/H_2$ were also carried out for comparison.

The experimental procedure and apparatus for this study were similar to those described elsewhere.[3,4,7] NH_3BH_3 was effused into a cylindrical chamber from its reservoir. H_2 could be used as a carrier gas, with its flow rate controlled by a mass flow controller (Horiba STEC, SEC-40M). The reservoir could be heated, but we did not use a heater in the present work and the reservoir was kept at room temperature. A butterfly valve was set between the reservoir and the chamber so that the NH_3BH_3 flow could be shut off. B_2H_6, diluted with He to 2.0%, was introduced into the chamber through a mass flow controller (Horiba STEC, SEC- 410NC). The vacuum chamber was evacuated with a turbomolecular pump (Osaka Vacuum, TG350FCWB) backed by a dry scroll pump (Ulvac, DIS-251). W wires (30 cm in length and 0.39 mm in diameter, Nilaco) were resistively heated with a DC power supply (Takasago, EX-1125H2) and were exposed to a mixture of H_2 and one of the boron compounds, NH_3BH_3 or B_2H_6, to be boronized. The wire temperature was measured with a two-wavelength thermometer (LumaSense Technologies, ISR 12-LO) and kept at 2.29×10^3 K during the boronization and the B-atom density measurement.

B-atom densities were measured as a function of time after the termination of the boron-compound supply, using a laser-induced fluorescence technique at 249.77 nm, which corresponds to the $2s^2 3s\ ^2S_{1/2}$ - $2s^2 2p\ ^2P_{3/2}$ transition. The laser wavelength was scanned around the resonance line at 5-min intervals to evaluate B-atom density. 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-BaB$_2$O$_4$ (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). Absolute densities were evaluated by comparing the signal intensities with that of a known amount of B atoms obtained in a B$_2$H$_6$/He/H$_2$ system. In the measurements of the H$_2$ flow rate dependence and the wire temperature dependence of the B-atom densities, the laser wavelength was fixed at 249.77 nm and the photomultiplier signals were processed with a digital oscilloscope (LeCroy, HDO4032).

H$_2$ (Japan Air Gases, 99.999%), B$_2$H$_6$ (Takachiho Kako, diluted with He to 2.0%), and He (Japan Air Gases, 99.999%) were used from cylinders without further purification. NH$_3$BH$_3$ was obtained from Aldrich and the purity was 98.3%.

Figure 1 shows the time dependences of B-atom densities in the presence of a H$_2$ flow of 20 sccm (1 sccm = 6.9×10^{-7} mol s^{-1}), measured after boronization by NH$_3$BH$_3$/H$_2$. A virgin wire was boronized for 60 min or 60 s in the presence of ca 0.01 Pa of NH$_3$BH$_3$ and 2.1 Pa of H$_2$. The H$_2$ pressure during the B-atom density measurement was also 2.1 Pa. The wire temperature was kept at 2.29×10^3 K during both the boronization and the B-atom density measurement. No B atoms could be detected before the boronization, showing that the production of B atoms from H atoms and boron compounds deposited on chamber walls is minor. The B-atom density increased

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slightly at first and then became almost constant when boronized for 60 min as is shown in Figure 1. The initial increase was more remarkable when the boronization time was 60 s, while it was much less prominent when boronized for 120 min (not shown in Figure 1). The cause of the initial increase may be related to changes in surface morphology. It should be noted that B-atom ejection continues for more than 30 min even under the 60-s boronization. The absolute densities were evaluated by comparing the signal intensities with that obtained under the following conditions: flow rates of B_2H_6/He and H_2 were 10 and 20 sccm, respectively, total pressure was 3.9 Pa, and W wire temperature was 2.05×10^3 K. The B-atom density under such conditions has been determined to be 2.1×10^{11} cm^{-3}.[7] In the absolute density evaluation, it may not be possible to avoid uncertainty by a factor of two, but the random error in the relative values was less than 5%. Similar results were obtained when W wires were boronized by B_2H_6/He/H_2. B-atom density increased slightly and then decreased gradually with time. The absolute B-atom density was similar to that for NH_3BH_3, and was higher than that reported in our previous paper, 1.1×10^{11} cm^{-3}.[4] This difference can be ascribed to the difference in boronization temperatures. In the present work, W wires were boronized at 2.29×10^3 K, while the temperature was typically 2.05×10^3 K in Ref. 4. W wires are boronized more at higher temperatures.

Figure 2 shows the H_2 flow rate dependence of the B-atom density released from a boronized wire. The measurements were carried out while keeping the total pressure constant at 2.1 Pa by introducing He. Correction for the quenching of $B(2s^2 3s \ ^2S_{1/2})$ by H_2 is not necessary because of its short radiative lifetime.[12] The B-atom density increased almost linearly up to 6 sccm and then

showed partial saturation.　The density in the absence of a H_2 flow was 1/5 of that in the presence of a flow of 20 sccm.　This can be explained by considering that not only B atoms but also BH_x ($1 \leq x \leq 3$) are released from boronized wires and BH_x species are converted to B atoms by reactions with H atoms formed from H_2.[7]

The B-atom density showed an Arrhenius-type dependence against wire temperature, as is illustrated in Figure 3.　The apparent activation energy, measured in the presence of a H_2 flow of 20 sccm, was 3.67×10^2 kJ mol^{-1}.　This should include the contributions of both the activation energies to produce BH_x ($1 \leq x \leq 3$) and H atoms, the latter of which is 2.4×10^2 kJ mol^{-1}.[5,6]

The release of NH_x ($0 \leq x \leq 3$) species from W wires treated with NH_3BH_3 must be minor.　It is possible to detect NH and NH_2 radicals when W wires are heated in the presence of NH_3.[9]　These signals, however, disappear when the NH_3 flow is stopped.　In addition, permanent changes in electric resistivity are not observed when W wires are heated in the presence of NH_3.　These results strongly suggest that W wires are not nitrided by NH_3.　Since the NH_3BH_3 bond is very weak, 98 kJ mol^{-1}, and this bond should be broken at the first stage,[3] the nitridation of W wires must also be minor for NH_3BH_3.

Although W wires are not nitrided or phosphided,[13] carburization has been reported widely.[14-18] Winters et al. have reported that C atoms are released from carburized W wires when heated in the absence of any buffer gases, while CH_x ($x \geq 1$) species are not.[16]　It was also shown that the addition of H_2 (D_2) has no effect on the released C-atom densities.　This is in contrast to the present result that H_2 enhances the production of B atoms.　In the release of C atoms, simple evaporation should

be the main source,[16] while direct release of B atoms is rather minor for boronized tungsten. H atoms may play roles not only in the production of B atoms from BH_x ($1 \leq x \leq 3$) in the gas-phase, but also in the enhancement of the chemical processes to populate BH_x on wire surfaces.

Boronization without a H_2 flow was also tried, but the rate was very slow. H_2 must play a part in the boronization besides the B-atom formation in the gas-phase. NH_3BH_3 can be decomposed well even in the absence of a H_2 flow, but the production of B atoms is minor.[3,4] In other words, NH_3BH_3 should be decomposed to NH_3 and BH_3 on wire surfaces, but the H-atom density in the gas phase is too low to produce B atoms efficiently. The slow boronization in the absence of H_2 suggests that BH_x ($0 \leq x \leq 2$), presumably B, is responsible for the boronization and BH_3 plays only a minor role.

The B-atom density obtained under the present conditions is more than enough for surface doping. The B-atom density in the gas phase obtained in the present work, on the order of 10^{11} cm^{-3}, is one order of magnitude less than that obtained in our previous work on the $B_2H_6/He/H_2$ system, where the B_2H_6 partial pressure was 0.026 Pa.[7] In the catalytic doping of B atoms to silicon substrates, however, the wire temperature is typically less than 1.6×10^3 K,[1,2] and the estimated B-atom density required is less than 10^9 cm^{-3}.

In conclusion, we present a novel technique to produce B atoms without using explosive boron compounds, such as B_2H_6. W wires can be boronized by a mixture of NH_3BH_3 and H_2 to be sinks for B atoms. Boronized wires are heated in the presence of neat H_2 to be sources of the B atoms. The release continues more than 4 h. The B-atom density in the gas phase can be increased more

than 10^{11} cm^{-3}, which is sufficient for surface doping. Since the W wires are hardly nitrided, contamination by N atoms is not expected, if the substrates are installed after the boronization.

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Figure captions

Figure 1. Time dependences of B-atom densities in the presence of a H_2 flow of 20 sccm measured after boronization. Boronization was carried out for 60 min (closed circle) or 60 s (open circle) in the presence of ca 0.01 Pa of NH_3BH_3 and 2.1 Pa of H_2, while the B-atom density was measured in the presence of 2.1 Pa of neat H_2. The wire temperature was kept at 2.29×10^3 K during both the boronization and the B-atom density measurement.

Figure 2. H_2 flow rate dependence of B-atom densities released from a boronized W wire. The total pressure was kept at 2.1 Pa by introducing He. The wire temperature was 2.29×10^3 K .

Figure 3. B-atom densities as a function of the reciprocal of boronized W wire temperature measured in the presence of 2.1 Pa of H_2.
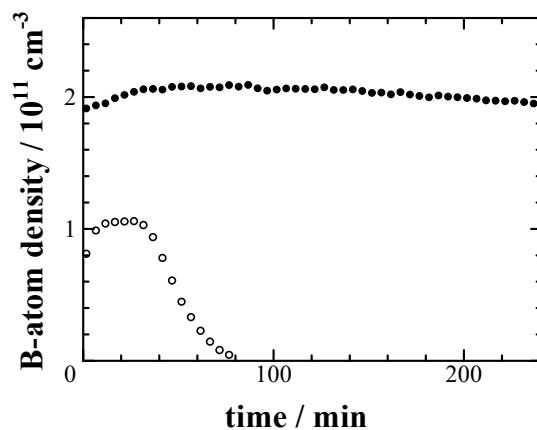
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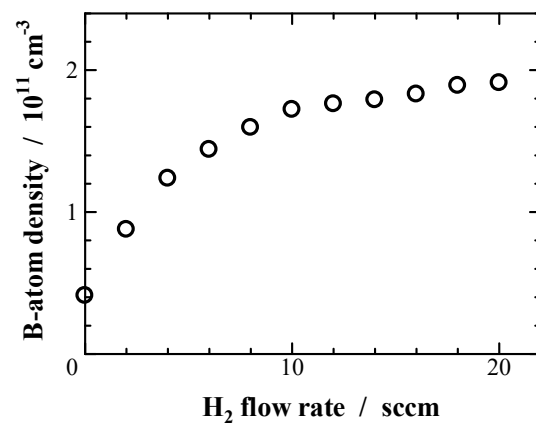
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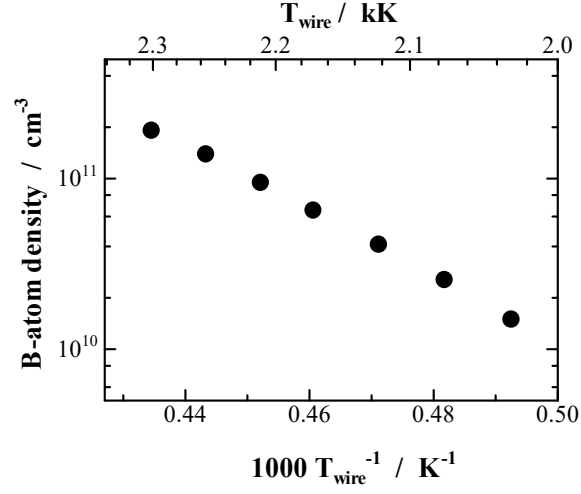
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