Effect of crucible materials for liquid Si diffusion measurements

T. Fukazawa[a], M. Kaneko[a], M. Uchida[b] and K. Terashima[c]

a) Space Department, Ishikawajima Jet Service Co.Ltd.
b) National Space Development Agency of Japan
c) Shonan Institute of Technology

ABSTRACT

In order to choose a crucible material for liquid Si diffusion experiments, a boron nitride (BN) and pyrolytic boron nitride (PBN) were examined. The Si sample was heated in a BN and a PBN crucible, and the concentrations of B and N were analyzed. The concentration of B amounted to 5 – 8 x 10^{19} atoms/cm^3 even after the sample was held at just above the melting point (1713 K) for a short period (10 minutes). N concentration was about 2 x 10^{17} atoms/cm^3, that is 2 orders smaller than B concentration. The reaction of the Si sample to BN or PBN crucible was not observed.

1. INTRODUCTION

Silicon (Si) is the most important and basic semiconductor in recent years. To make a silicon crystal of high quality and large diameter, the diffusion coefficient in its liquid is required. However, since liquid Si has high reactivity, it is hard to choose a crucible material. The wetability tests were performed by one of the authors [1] and it was found that BN had poor wetability to Si melt. Therefore, boron nitride (BN) can be thought to be a candidate of the crucible materials for liquid Si diffusion experiments. However, it needs to know the reactivity between liquid Si and BN, and how much amount of boron and nitrogen melts into Si. BN and pyrolytic boron nitride (PBN) crucibles were examined in this study.

2. EXPERIMENTAL

A silicon sample was put in a BN or a PBN crucible, as shown in Fig. 1. The crucible was covered with a graphite cell to prevent liquid Si from spilling. The crucible and the graphite cell had holes to exchange the atmosphere in the crucible. The sample was heated up to 1713 K and 1743 K (only 1743 K for PBN experiments) with the holding time of 10, 90 and 180 minutes. The argon gas was flown at 2 l/min in order to avoid Si oxidation. The temperature was measured by a thermocouple in a graphite cell during experiments. The samples after the experiments were analyzed by the Secondary Ion Mass Spectroscopy (SIMS).

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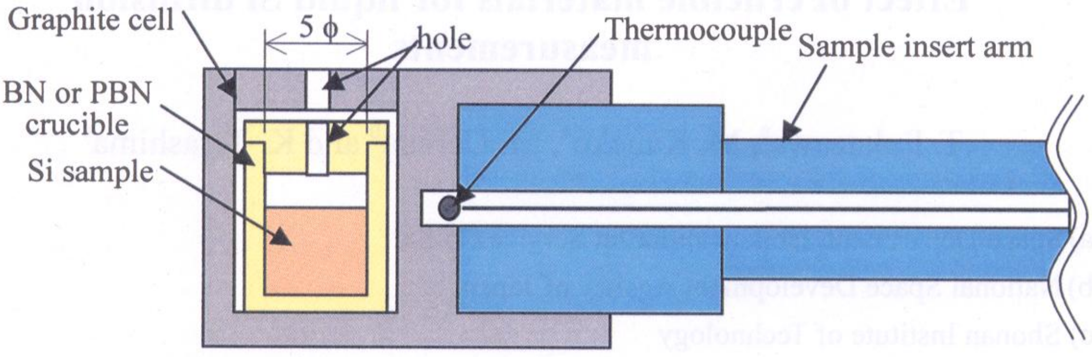
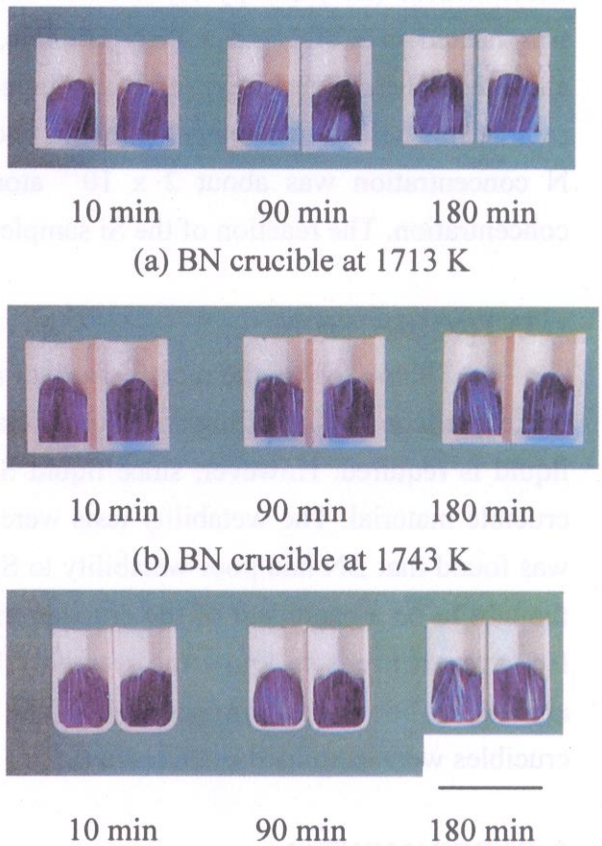


Figure 1　Sample configuration of reactivity test between Si and BN crucible

3. RESULTS AND DISCUSSION

The samples after the experiments were cut parallel to the sample axis. The samples and crucibles didn't have any cracks, as shown in Fig. 2. The Si samples became convex shape on the upper surface because of solidification expansion, and it means that the samples melted completely in all experiments. Figure 3 shows the boundary of the BN crucible and the Si sample after the experiment at 1743 K for 180 minutes. There was a gap between the sample and the bottom of the crucible, which may be caused by the sample shrinkage with the decrease of temperature. Any evidence of the reaction was not observed in all experiments.



(a) BN crucible at 1713 K

(b) BN crucible at 1743 K

(c) PBN crucible at 1743 K

Figure 2　Samples after experiments with holding time of 10, 90 and 180 min.

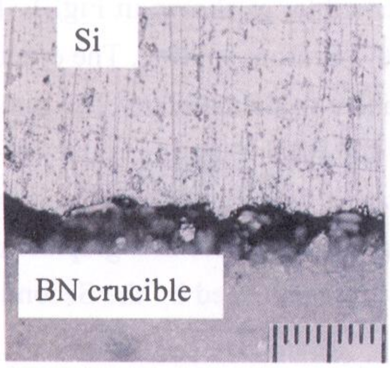


Figure 3　Boundary between Si and bottom of BN crucible after experiment at 1743 K for 180 min.

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The SIMS analysis of the unheated sample and the samples after the experiments were carried out by Sumika Chemical Analysis Service. In order to analyze B, N and O concentrations at once, the Cs^+ ion was selected as the sputtering ion. The sample was analyzed at each depth until the B, N and O concentrations became constant. Figure 4 shows 9 analysis points of each sample.

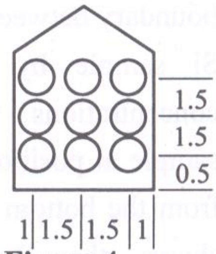

Figure 4 Analysis points (unit: mm)

The B, N and O concentrations of the unheated sample were less than 5 x 10^{15}, 5 x 10^{15} and 5 x 10^{16} atoms/cm^3, respectively. The O concentration was under the detectable level (5 x 10^{16} atoms/cm^3) in all samples. The B and N concentration distributions in samples were almost homogeneous with a large scatter. The concentrations of B and N near the crucible were found to be never large.

Figure 5 shows the average B concentrations after the experiments. The B concentration was 5.3 – 7.5 x 10^{19} atoms/cm^3 for BN crucible, and was not so much affected by temperature and time variation. It was 7.8 – 8.4 x 10^{19} atoms/cm^3 for PBN crucible, which was slightly larger than BN ones, and the value was almost constant with the variation of holding time.

Figure 6 shows the average N concentration after the experiments. It was 1 – 2 x 10^{17} atoms/cm^3 for BN crucible, and was almost the same value in all samples even if the temperature and the time were different. The N concentration for the PBN crucible was larger at longer holding time, 2.6, 4.8 and 12 x 10^{17} atoms/cm^3 for 10, 90 and 180 minutes, respectively. The N concentrations for both BN and PBN crucible experiments were in order of 10^{17} atoms/cm^3, which was 2 orders smaller than B concentration. It was sometimes observed on the SIMS analysis that N concentration became very large when the vacuum level became bad. It can be considered that the N_2 gas might be included in the frozen samples at the room temperature.

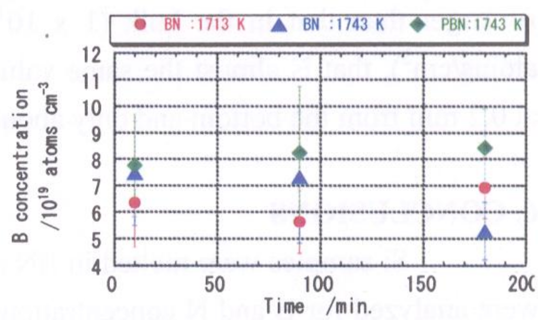

Figure 5 B concentration after experiments as a function of holding time

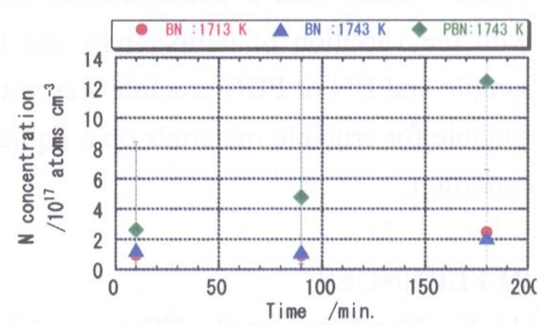

Figure 6 N concentration after experiments as a function of holding time

Even though it was hard to analyze the concentration near the

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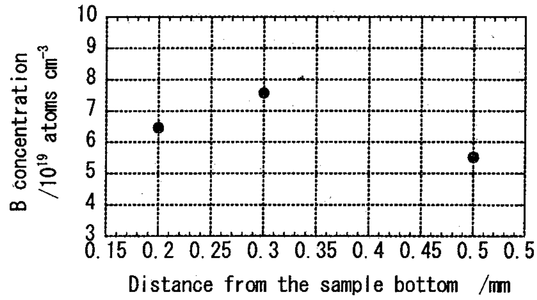
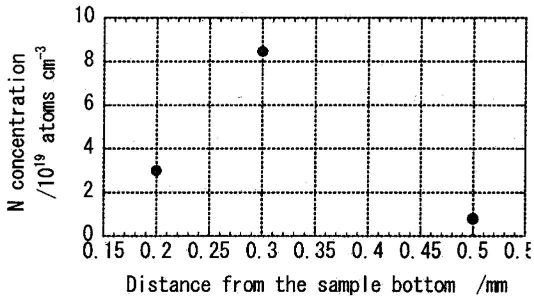
boundary between the BN crucible and the Si sample by SIMS, the B and N concentrations were measured in Si sample at positions 0.2 and 0.3 mm away from the bottom of the crucible. Figure 7 shows the B and N concentration distributions near the boundary for the sample kept in the BN crucible at 1743 K for 180 minutes. The B concentration near the boundary (0.2 and 0.3 mm from the bottom) was almost the same as the value in the bulk, about 6 x 10^{19} atoms/cm^3. It was expected that the N concentration near the boundary should be large to make Si_3N_4 because the N concentration in the bulk was 2 orders smaller than B concentration. However, the N concentration near the boundary was not so larger than that in the bulk (1 x 10^{19} atoms/cm^3), that is almost the same value at 0.2 mm from the bottom and only about 4 times at 0.3 mm (in the same order).



(a) B concentration



(b) N concentration

Figure 7 B and N concentrations near edge (boundary between Si and BN crucible) after 1743 K 180 minute experiment

6. CONCLUSIONS

Si samples were melted in BN and PBN crucibles and their solidified samples were analyzed for B and N concentrations. B concentration in Si was saturated at 5 – 8 x 10^{19} atoms/cm^3 even for the experiment at just above the melting point (1713 K) for a short period (10 minutes). N concentration was about 2 x 10^{17} atoms/cm^3, that is 2 orders smaller than B concentration. Since the B and N concentrations didn't change with the variation of temperature and holding time and the reaction between the Si sample and BN or PBN crucible was not observed, BN and PBN were considered to be suitable for crucible materials on a liquid Si diffusion experiment under B and N doped condition.

REFERENCES

[1] K. Terashima, et.al., "The wetability and reaction of liquid silicon to various refractory materials", NASDA Technical Memorandum ISSN 1345-7888 NASDA-TMR-000013E "Modeling and Precise Experiments of Diffusion Phenomena in Melts under Microgravity Annual Reports 1998 and 1999", pp.125-129

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