A sealing technique of the shear cell method for diffusion measurements on high vapor pressure liquids

Tomoharu Fukazawa*[1], Minoru Kaneko*[1], Akira Tanji*[2], Tadahiko Masaki*[3] and Misako Uchida*[3]

*1 Space Department, Ishikawajima Jet Service Co., Ltd.

*2 Space Experiment System Department, Ishikawajima-Harima Heavy Industries Co., Ltd.

*3 Space Utilization Research Center, National Space Development Agency of Japan

Abstract

A sealing technique of the shear cell method was developed for liquid diffusion measurements of high vapor pressure materials. Some experiments were carried out to confirm the availability of B_2O_3 for sealing and to check the transmissivity of a sample vapor through a boron nitride crucible. After some experiments, a shear cell with sealing mechanism was produced experimentally, and a diffusion experiment with this shear cell was performed.

Introduction

The shear cell method is one of the experimental methods of liquid diffusion measurements, which has the following advantages; heating and cooling process aren't included for measurements, and solidification process doesn't affect on measurements. Especially, a sample, which expands on solidification, needs this shear cell method for liquid diffusion measurements. However, since the shear cell consists of some thin disks, the sample can evaporate through the slight gap of the disks and it is hard to measure diffusion coefficients of high vapor pressure liquids, for example, compound semiconductors, such as GaAs. We tried to realize the idea to employ B_2O_3, which is used for the GaAs crystal growth process to prevent the evaporation of As, for the sealing of a shear cell. First, we performed the following investigations to confirm the sealing mechanism.. After these investigations, we produced a shear cell with a sealing mechanism and carried out a diffusion experiment using the shear cell.

The change of evaporation rate with temperature

The weight change of PbTe and InAs was measured by TG-DTA (thormogravimetric and differential thermal analysis). The samples were put in boron nitride crucibles, and heated up to 960 and 1000 degree C for PbTe and InAs, respectively, with Ar gas flow at 100 ml/min. One case was covered with B_2O_3, as shown in Figure 1, and the other case was without B_2O_3.

PbTe sample started to evaporate at 800 degree C and the weight rapidly decreased over the melting temperature, 920 degree C. After the sample was kept at 960 degree C for 10 minutes, the sample weight decreased about 6 % for the case without B_2O_3. The weight change of the sample covered with B_2O_3 was 4.9 %. It was observed that the PbTe sample blew out from the B_2O_3. InAs sample started to evaporate at 550 degree C and the weight rapidly decreased at 900 degree C. The weight change was 15.6 % and 10.8 % for a sample with and without B_2O_3, respectively. It was confirmed that the B_2O_3 was effective to prevent InAs from evaporation.

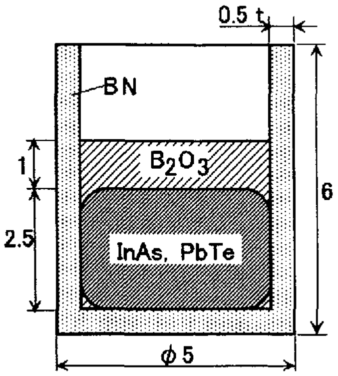


Figure 1 Sample configuration for TG-DTA measurements

Confirmation of the effect of B_2O_3 for sealing

Figure 2 shows the sample configuration of the experiments to confirm the effect of B_2O_3 for sealing. The PbTe, SnTe and InAs samples were respectively put in boron nitride (BN) crucibles covered with B_2O_3, and sealed in quartz ampoules with Ar gas of 200 torr or in vacuum. The experiments without B_2O_3 were also performed to compare the results. The sample was heated respectively up to 900 degree C for SnTe and to 1000 degree C for PbTe and InAs for 1 hour. In order to soften the B_2O_3 and cover the sample with B_2O_3 well, the sample was kept at 500 degree C for 10 minutes during heating. The upper part of the ampoule was kept at 300 degree C to simulate the shear cell method.

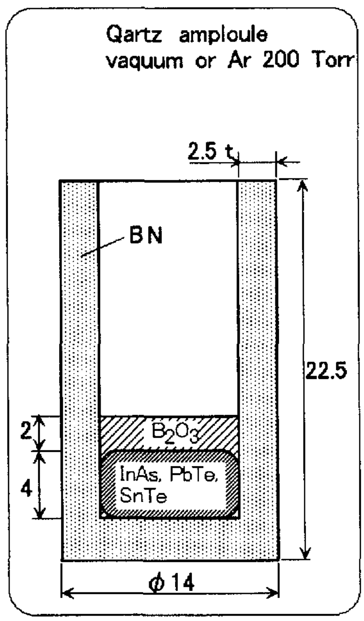
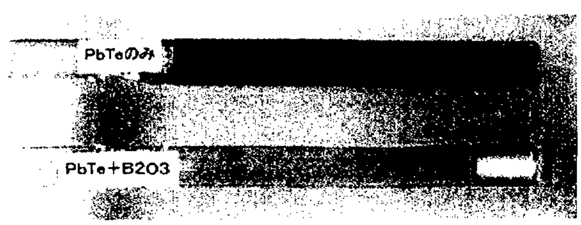


Figure 2 Sample configuration to confirm the B_2O_3 effect on sealing

The ampoule after the experiment was blackened by the sample vapor, as shown in Photograph 1. The color of the ampoule without B_2O_3 is darker than that with B_2O_3. Table 1 shows the results of the weight change experiment. The evaporation ratio reduced to less than 1 % if the B_2O_3 was used for sealing. The availability of B_2O_3 for sealing was confirmed.



Photograph 1 Ampoule after the experiment (upper : PbTe, lower : PbTe with B_2O_3)

The B_2O_3 after the experiment was analyzed at the position of 1.0 mm distant from the metallic compound sample by

EPMA (Electron Probe Microanalyzer) to check if the liquid sample dissolved in liquid B_2O_3. It was confirmed that SnTe and InAs didn't dissolve in B_2O_3 with the concentration of less than 0.1 %. The concentration of PbTe was observed to be about 0.1 %, and it was concluded that PbTe slightly dissolved in B_2O_3.

Table 1 Experimental conditions and evaporation ratio after the experiments

Sample	Temperature /degree C	Time /hour	Atomosphere	Evaporation ratio /%
SnTe	900	1	Ar 200 torr	1.034
SnTe+ B_2O_3	900	1	Ar 200 torr	0.717
PbTe	1000	1	Ar 200 torr	3.756
PbTe+ B_2O_3	1000	1	Ar 200 torr	0.833
InAs	1000	1	Ar 200 torr	19.031
InAs+ B_2O_3	1000	1	Ar 200 torr	0.371
InAs	1000	1	Vacuum	33.333

Transmissivity of a sample vapor through boron nitride(BN)

The transmissivity of boron nitride crucibles was examined. Two kinds of boron nitride, UHS-FL (transmissivity of 20 ml/min/cm^2) and UHF-D (no-transmissivity), were used for the experiments with two kinds of thickness, 0.5 mm and 1.0 mm. Figure 3 shows the sample configuration to measure the weight change only through the BN crucible. The InAs sample was covered with BN crucible, and B_2O_3 was put between inner and outer crucibles in order that the sample can not come out from the gap of the inner and outer crucibles. The crucible was sealed in a quartz ampoule with 200 torr Ar gas or in vacuum. The InAs sample was kept at 1000 degree C for 1 hour. The sample was kept at 500 degree C for 10 minutes during heating to soften the B_2O_3.

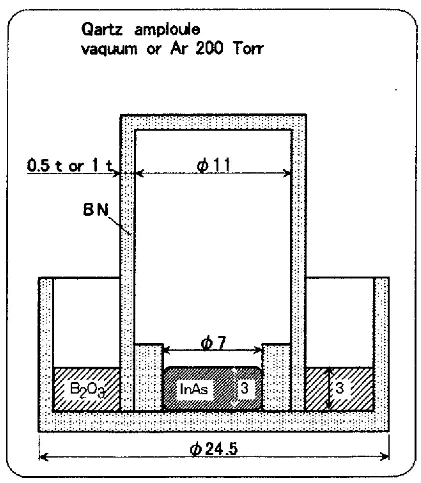


Figure 3 Sample configuration of the transmissivity experiments

It was confirmed that the weight change was small when the Ar gas was introduced in the quartz ampoule as shown in Table 2.

Table 2 Results of the BN transmissivity experiments

BN material	BN thickness /mm	Atmosphere	Evaporation ratio /%
UHS-FL (transmissivity of 20 ml/min/cm^2)	0.5	Vacuum	23.327
	1.0	Vacuum	23.091
	0.5	Ar 200torr	17.679
	1.0	Ar 200torr	16.580
UHS-D (no transmissivity)	1.0	Ar 200torr	17.021

However, the difference of the weight change wasn't observed for the different thickness (0.5 mm and 1.0 mm, respectively) and for the different kinds of BN materials (with transmissivity of 20 and 0 ml/min/cm^2, respectively).

A shear cell experiment with the sealing mechanism

Figure 4 shows the schematic illustration of the shear cell with sealing mechanism. Photograph 2 shows the shear cell used in the present experiment. Each shear cell disk had a groove, on which B_2O_3 was put in order to seal the gap between the disks. B_2O_3 was also put at the sample ends. The cell was made of boron nitride and the rotation shaft was made of tantalum. The three diffusion couples of $Pb_{0.7}Sn_{0.3}Te$ and $Pb_{0.8}Sn_{0.2}Te$, which were 1.5 mm diameter and 12 mm length each, were used for the experiment. A diffusion experiment was carried out at 1000 degree C for 4 minutes with He gas by using the large isothermal furnace in NASDA.

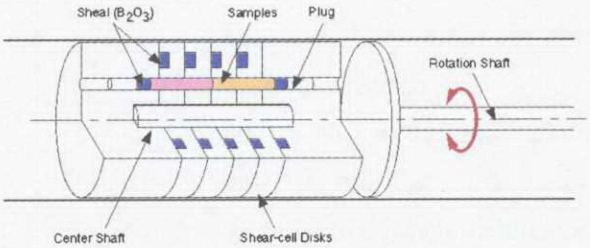
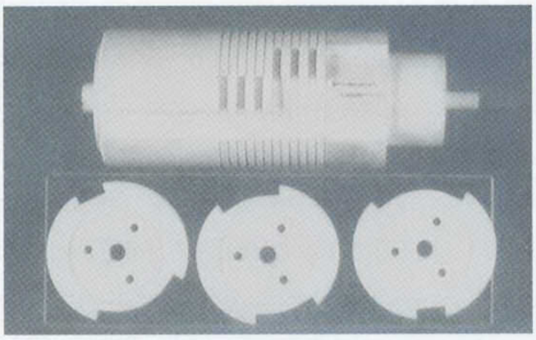


Figure 4 Schematic illustration of the shear cell with sealing mechanism



Photograph 2 The shear cell with sealing mechanism used in the experiment

The samples were successfully joined, but weren't completely divided into small pieces because the rotation shaft was bent slightly. The sample weight reduction was 7, 8 and 19 %, respectively for three diffusion couples. It was observed that the B_2O_3 spread all over the disks, and that the samples blew out from the B_2O_3 at the sample ends. It was considered that the sample blew out probably because the pressure inside of the shear cell became higher due to the sample vapor than the atmosphere in the quartz ampoule and B_2O_3 couldn't support this pressure difference.

Conclusions

The availability of the B_2O_3 and the transmissivity of sample vapor through boron nitride crucible was investigated, and the shear cell with sealing mechanism was developed. It was confirmed that the B_2O_3 was effective to prevent high vapor pressure sample from evaporation, and the sample could come out through the boron nitride even with the no-transmissivity. Some tests with other material would be needed to develop the sealing mechanism for the shear cell.