Development of shear cell for liquids with high vapor pressures

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Abstract

To establish the shear cell technique for the diffusion coefficient measurement of high vapor pressure sample, the seal effect of B_2O_3 melts was investigated by using a simplified shear cell unit. Moreover, the seal effect was investigated by using a short form shear cell. Even for liquid samples with high vapor pressures, the seal effect of B_2O_3 can be expected.

1. Introduction

For the technical development of the diffusion experiment for melts of semiconductor material in the fiscal year, the sealing effect of B_2O_3 melts at a high temperature was studied; glassy carbon (GC) and pyrolytic boron nitride (PBN) were employed as cell materials and InAs as a liquid sample with high vapor pressure. Moreover, a short form shear cell was prepared by using the GC material and PBN material for InAs melts. Investigation was performed for the ability as shear cell and the seal effect.

2. Test of sealing effect at high temperatures by the simplified shear cell units

2.1 Experimental

The simplified shear cell unit was designed and tested. It consisted of two disks of shear cell, which had groove to put B_2O_3 ring (thick=0.8mm, width=1.5mm) and a space for sample (InAs and Ge), as shown in Figure 1. Simplified shear cell unit was made of GC, PBN and graphite with pyrolytic graphite (PG) coating. They were fixed by Ta wire, after the sample and the B_2O_3 ring were set inside them.

The effect of surface roughness was also investigated for GC in the roughness range from #600 to #3000.

The sample in the simplified shear cell unit was kept at 773K for 30min in vacuum to soften the B_2O_3 ring, then heated up and kept at 1473K(InAs sample) or 1823K(Ge sample) in an Ar atmosphere of 380Torr ~ 1140Torr for 1 hour, as shown in Table 1. The adopted experimental configuration for this purpose was shown in Figure 2. After it was cooled in the furnace, the weight change of sample was measured.

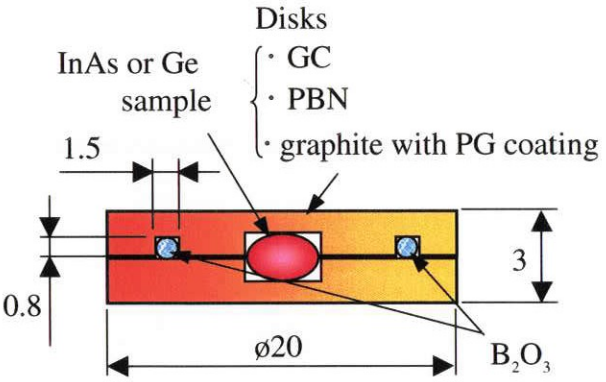


Fig.1 Sample configuration of simplified shear cell unit

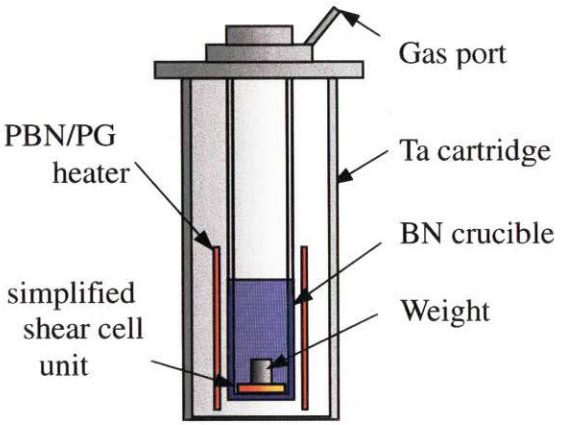


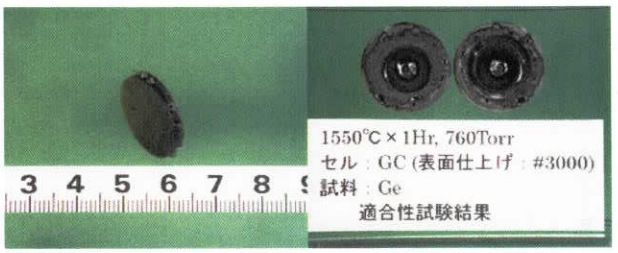
Fig. 2 Test configuration

2.2 Results

(1) Appearance inspection

(a) The simplified shear cell unit made of GC

Figure 3 shows the simplified shear cell unit after the experiment. Sealing material of B_2O_3 leaked out between each disk for both InAs and Ge samples (Figure 3(a)). But, the GC disk didn't react to InAs and Ge. In fact, the InAs sample could be removed easily. However, the Ge sample could not be detached (Figure 3(b)).



(a) (b)

Fig. 3 The simplified shear cell unit made of glassy carbon after experiment

(b) The simplified shear cell unit made of PBN and graphite with PG coating

The PBN disks and graphite ones with PG coating didn't react to InAs, Ge and B_2O_3 and were not found to be damaged after experiments.

(2) Weight change

Results of weight change of sample are shown in Table 1.

(a) InAs sample

The weight loss was less than 0.7% for the GC disks whose surface roughness was #3000 (Ra=0.17μm). The evaporation loss of InAs sample seemed to be absent for this surface condition. But, the weight loss amounted to about 2.1% - 11.5% for the GC disks whose surface roughness was Ra=0.45μm ~ #600 (Ra=0.64μm). Therefore, these surface conditions didn't prevent InAs from the evaporation, judging from the present simplified shear cell unit experiment.

The weight loss for the PBN disks amounted to about 6.6% - 14% and 1.3% in an Ar atmosphere of 760Torr and 1140Torr respectively. It amounted to about 3.8% - 8.6% for graphite disks with PG coating. These configurations didn't prevent the evaporation loss of InAs.

(b) Ge sample

Without sealing material, B_2O_3, no weight loss was detected for the case of GC and PBN (Ar atmosphere of 760Torr), graphite with PG coating (Ar atmosphere of 360Torr). But, when the experiment was performed with the seal material, B_2O_3 for GC disks, the disk and Ge sample adhered each other and the weight of a sample could not be measured after experiments.

3. Sealing experiments at high temperatures by the short form shear cell

3.1 Experimental

As shown in Figure 4, the short form shear cell was set in the cartridge made of Ta, which could be evacuated and filled by Ar gas in the Large Isothermal Furnace (LIF) in National Space Development Agency (NASDA). In addition, the rotation rod of shear cell could be rotated from the outside of LIF.

Based on the results of Sec.2, the test of Ge sample was performed without using the seal material, B_2O_3, and that of InAs sample was done by using the seal material.

Two pieces of diffusion couple sample in the short form shear cell was kept at 773K for 30min in vacuum to soften the B_2O_3 ring, then heated up to 1473K(InAs sample) or 1823K(Ge sample) in an Ar atmosphere of 660Torr. After keeping at these experimental temperatures for 20min, the liquid diffusion couple was created by joining operation. After 1 hour, it was separated into small pieces. Then, the furnace cooling was performed and the weight change of sample was measured.

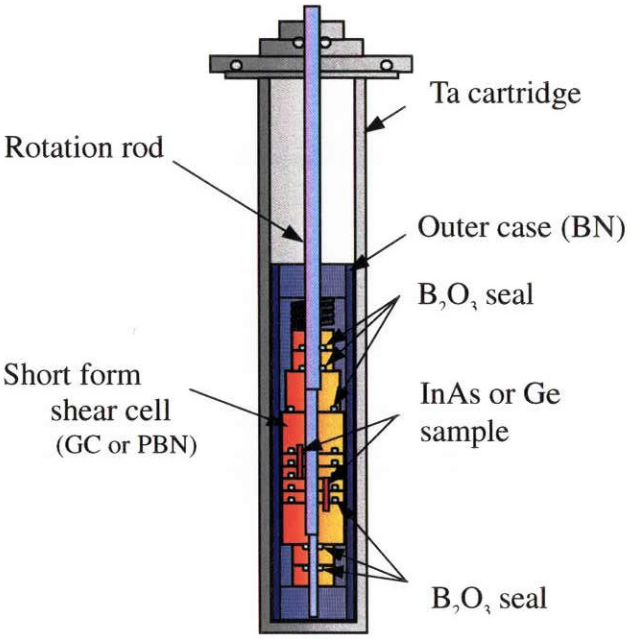


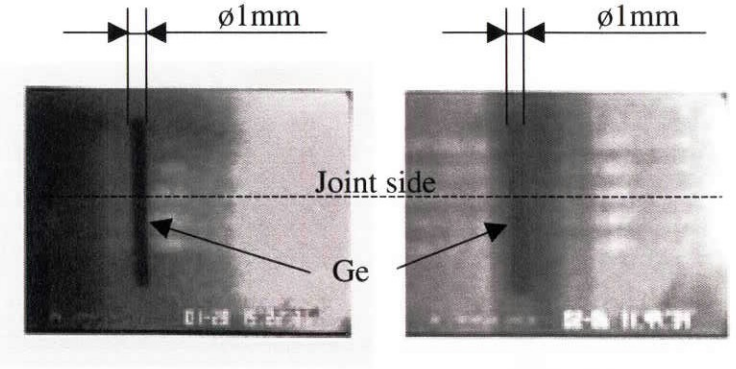
Fig. 4 Test configurations

Experimental conditions are shown in Table 2. The main experimental conditions are based on the experimental results of simplified shear cell unit in Sec. 2.2.

3.2 Results

(1) Observation of the alignment of diffusion couple sample

The alignment of diffusion couple of Ge sample was investigation by the in-situ X-ray observation system for the diffusion in liquid metals and alloys, which has been developed in NASDA by using the Advanced Furnace for microgravity Experiments with X-ray radiography (AFEX).



(a) GC (b) PBN

Fig.5 X ray photograph of Ge sample in short form shear cell

From the X ray photograph shown in Figure 5(a), it was confirmed that the short form shear cell made of GC had almost no misalignment between two pieces of diffusion couple sample. However, from the X ray photograph shown in Figure 5(b), that made of PBN resulted in about 100micrometers misalignment between two pieces of diffusion couple sample

(it is about 10% of diameter 1mm of a sample).

(2) Appearance inspection

・PBN or GC + Ge sample

No particular abnormalities were observed for the case of PBN and GC by the appearance inspection, and the sample was cut successfully on the shear operation. All cells were tightly filled with the sample due to the solidification expansion. The Ge sample was not able to be detached from the thick cell, especially in the case of both ends.

・PBN or GC + InAs sample

PBN and GC disks of the shear cell and the outer case made of BN adhered each other by the seal material, which leaked out between disks, although otherwise no particular abnormalities were observed. On decomposing the shear cells by soaking in water, no broken parts were observed and all samples in these cells were recovered.

(3) Results of weight measurement

Results of weight measurements are shown in Table 3. Fundamentally, the amount of evaporation of a sample should be evaluated from the weight change of sample itself. Therefore, when the sample was able to be taken out finely, the evaporation ratio was estimated in this manner. However, if impossible, it was estimated from the weight change of shear cell containing sample between before experiment and after one.

・Ge sample

The evaporation ratio of Ge in the case of short form shear cell made of GC was 1.37%, which is 4 times larger than the experimental result of simplified shear cell unit made of the same material. This may be derived from the increase of surface area in the former case compared with the latter case.

・InAs sample

The evaporation ratio of InAs in the case of short form shear cell was obtained to be respectively 6.77% for GC and 16.5% for PBN. Although, GC may be available for sealing the InAs vapor, the evaporation rate is 10 times larger compared with experimental result of the simplified shear cell unit. The large evaporation loss for PBN may be attributed to the evaporation at the holding temperature of 873K before heating up to the experimental temperature, 1473K. In addition, introduced Ar gas might break

the B_2O_3 seal. In the present short form experiment, the employed InAs and Ge samples were small and light. In addition, due to the volume expansion on solidification, some small pieces of samples may disappear among shear cell disks and may be not recovered on the shear cell decomposition. These may results in an error on the evaluation of the evaporation loss.

4. Conclusions

(1) The followings were obtained in the simplified shear cell unit experiments.

By combining the cell made of GC (surface finish #3000) and B_2O_3 seal material, the evaporation of an InAs sample can be prevented at the temperature of 1473K and Ar atmosphere pressure of 760Torr. Even if the seal material of B_2O_3 in not used, the evaporation of Ge sample can be suppressed at 1823K and Ar pressure of 360Torr with the use of simplified shear cell units made of GC, and PBN and graphite with PG coating.

(2) The followings were obtained in the short form shear cell experiments.

The evaporation ratio of InAs sample with B_2O_3 seal was measured at a temperature of 1473K and an Ar atmosphere pressure of 660Torr. In the experiments using the shear cell made of GC (surface finish #3000), there was 6.8% (2.5mg) weight reduction. Moreover, in the shear cell made of PBN, there was 16.5% (9.1mg) weight reduction. The evaporation ratio of Ge sample was measured at a temperature of 1823K and an Ar atmosphere pressure of 660Torr. In the experiment using a shear cell made of GC (surface finish #3000), there was 1.4% (0.9mg) weight reduction.

Table 1 Weight change after sealing test using simplified shear cell units

Material	Sample	Temp. [K]	Press. [Torr]	B_2O_3 seal	Sample weight [g]		Weight change [g]	Evaporation rate [%]
					before	after		
GC(#3000)	InAs	1473	760	○	0.1027	0.102	0.0007	0.682
GC(#3000)			760	○	0.0912	0.0908	0.0004	0.439
GC(#600)			760	○	0.1036	0.0917	0.0119	11.486
GC(#600)			760	○	0.091	0.0909	0.0001	0.110
GC(#600)			760	○	0.1159	0.1123	0.0036	3.106
GC(Ra0.45μm)			760	○	0.1029	0.1007	0.0022	2.138
PBN			760	○	0.0997	0.0857	0.0140	14.042
PBN			760	○	0.1045	0.0967	0.0078	7.464
PBN			760	○	0.1032	0.0966	0.0066	6.395
PBN			1140	○	0.0832	0.0821	0.0011	1.322
PG coat			760	○	0.0987	0.0949	0.0038	3.850
PG coat			760	○	0.1003	0.0917	0.0086	8.574
GC(#3000)	Ge	1823	760	○	0.0935	reacted	impossible	–
GC(#3000)			760	○	0.0979	reacted	impossible	–
GC(#600)			760	×	0.1009	0.1006	0.0003	0.297
PG coat			760	×	0.0901	0.0901	0.0000	0.000
PG coat			380	×	0.0901	0.0901	0.0000	0.000
PBN			760	×	0.0902	0.0902	0.0000	0.000

○ : B_2O_3 sealing was adopted ; × : B_2O_3 sealing was not employed

Table 2 Experimental conditions

Materials	Sample	Temperature [K]	B_2O_3 seal	Atmosphere [Torr]
GC	InAs	1473	○	660(Ar)
	Ge	1823	×	
PBN	InAs	1473	○	
	Ge	1823	×	

○ : B_2O_3 sealing was adopted ; × : B_2O_3 sealing was not employed

Table 3 Estimated evaporation ratios

Sample	Temperature [K]	Material	Before [g]	After [g]	Weight change [g]	Evaporation ratio
InAs	1473	GC	0.0375	0.0350	0.0025	**6.77%**
		PBN	0.0549	0.0459	0.0091	**16.49%**
Ge	1823	GC	0.0681	–	–	**1.37%***
		PBN	0.0579	0.0552	0.0026	**4.56%**

* Estimated from the weight change containing sample