Diffusion measurements of Au in liquid Ag using high-precision shear cell method with *in-situ* X-ray observation system

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Abstract

In order to obtain the optimum way for the shear cell diffusion experiments, the investigation was performed for the factors minimizing the effect of the induced flow on joining a diffusion couple, such as the roughness of the shear cell disks, the shear velocity and the diffusion time. It was found that diffusion experiments should be performed using disks with rough surface at smaller shear velocity and that there is an optimum diffusion time for the diffusion experiments on the ground.

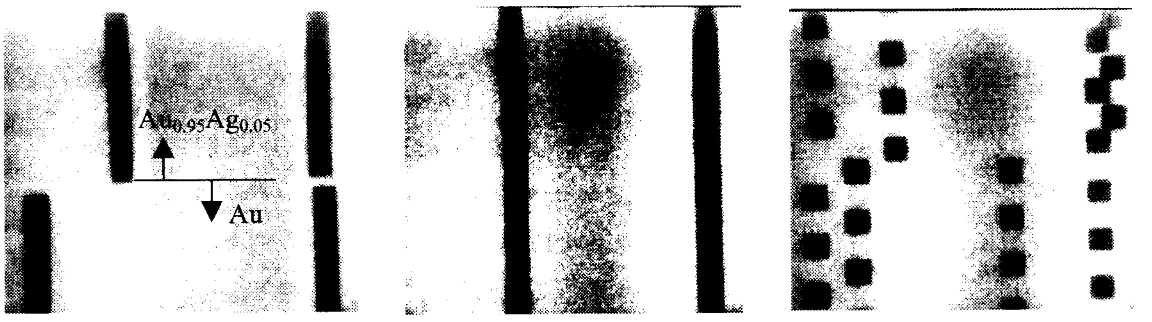
1. Introduction

Diffusion coefficients in liquid semiconductors are very important for the simulation of the crystal growth of semiconductors such as Si, GaAs, etc. But it is very difficult to measure those diffusion coefficients accurately because of their high temperature, high reactivity and high vapor pressure.

The shear cell method is known as a technique to measure diffusion coefficients accurately in liquids. A diffusion couple is separated during heating, joined at the aimed temperature, and divided into small pieces before cooling. Consequently, this method can remove diffusion during heating and cooling processes, and solidification effects[1)]. However, because of the complicated structure and the complicated movement of the shear cell, it has some problems. The first one, misalignment of a diffusion couple, has been solved by developing a new system using *in-situ* X-ray observation to confirm whether the diffusion couple joins accurately or not[2),3)]. The second one is the flow which occurs on joining the liquid samples. This report mentions about some experiments to minimize the effects of the flow on joining.

2. Experimental

"Shear cell" consists of 20-30 disks with a hole, rotation shaft, key bar and cartridge. Two diffusion couple of Ag and $Ag_{0.95}Au_{0.05}$, which was 1 mm diameter and 30 mm length (15 + 15 mm), was set in the shear cell. To join or to divide the diffusion samples, a stepping motor rotates a rotation shaft, and a key bar controls the rotating angle[3)]. Fig.1 shows an X–ray image of a diffusion couple. The upper sample was lighter sample, Ag, and the lower one was the heavier sample, $Ag_{0.95}Au_{0.05}$. At first, the diffusion couple was set separately in the shear cell (Fig.1 (a)). Then, the sample was heated up to the



(a) separated (b) joined (c) divided

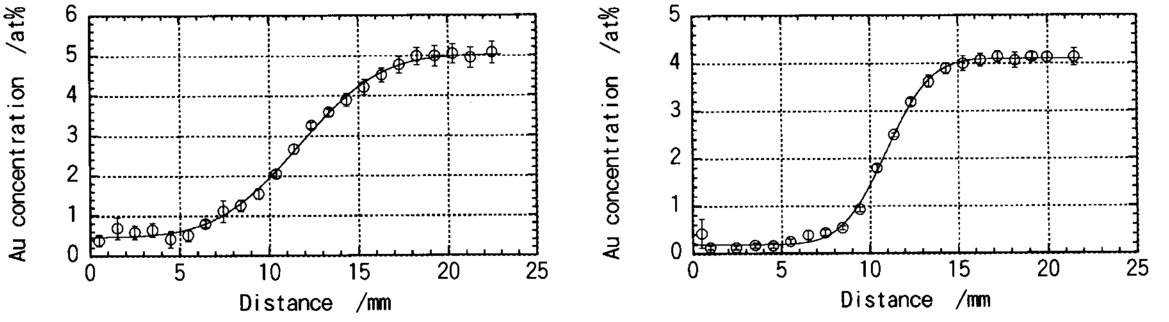
Fig.1 X-ray image of diffusion couple during experiment

diffusion temperature, 1273 K; the diffusion couple was joined (Fig.1 (b)); and finally, the diffusion couple was divided into 20-30 pieces after the diffusion time finished (Fig.1 (c)). The concentration profile was determined by EPMA (Electron Probe Micro Analyzer) on each piece.

To find the optimum way to minimize the flow on joining, the effects of (1) surface roughness of the shear cell disks, (2) shear velocity and (3) diffusion period were investigated. To examine the effect of the surface roughness (1), diffusion experiments were performed at 1273 K for 600 seconds by using shear cell disks with some differently polished surfaces. At first, the shear cell disks were grinded up to the grade of #600 emery paper to make them flat, and, then, they were finished with #100, #600 or #3000 emery paper or aluminum oxide beads, respectively. To prove the effect of shear velocity (2), diffusion experiments were carried out at 2.2 mm/s and 0.5 mm/s of rotation velocity with #100 finished shear cell disks at 1273 K for 600 seconds diffusion time. To search the effect of the diffusion period (3), diffusion experiments were performed with changing the diffusion time among 300 and 2400 seconds. They were conducted at 1273 K with #100 finished shear cell disks at 0.5 mm/s rotation velocity.

3. Results and discussion

The concentration distributions of Au after the diffusion experiments are shown in Fig.2. The



(a) #3000 (b) #100

Fig.2 Concentration distribution after diffusion experiments with #3000 and #100 finished shear cell disks respectively distributions were sound from the point of view of diffusion experiments. The diffusion layer seems to be larger for the large emery paper number, which shows smaller surface roughness. The effect of the surface roughness on the disks is shown in Fig.3. It was found that the diffusion coefficient was the smallest for #100 emery paper finished disks and its scatter was also the smallest. The diffusion coefficient was also small for aluminum oxide beads though its scatter is slightly large. The diffusion coefficient became larger with the increase of the emery paper number (smoother for the larger number). It can be considered that the friction of the disk and the induced flow become smaller with the increase of the roughness of the disk surface; a liquid sample is supported at points (not faces) if the disks are rough because of the bad wetness between the sample and the disks.

The effect of the shear velocity is shown in Fig. 4. The diffusion coefficients were (3.0 +/- 0.3) x 10^{-9} $m^{2/}s$ for 0.5 mm/s and (3.3 +/- 0.5) x 10^{-9} $m^{2/}s$ for 2.2 mm/s. The difference is within 10 %, but the diffusion coefficient and its scatter were a little smaller with slower shearing.

The effect of the diffusion time is shown in Fig.5. The diffusion coefficient was the minimum at 1800 s. When the diffusion time was longer, the obtained diffusion coefficient was larger

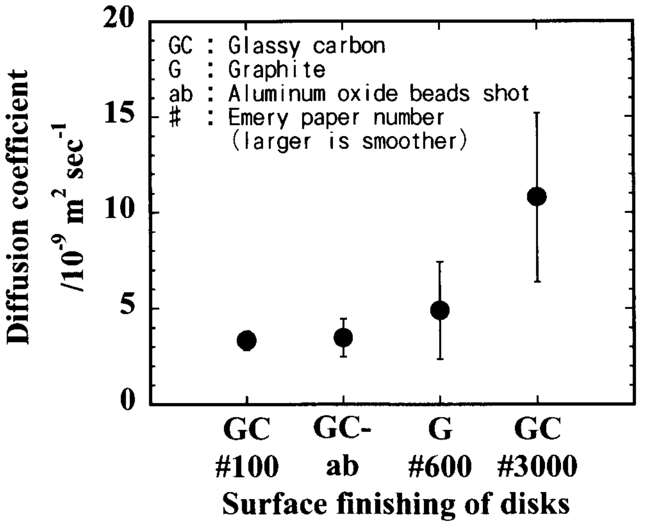


Fig.3 Effect of surface roughness of shear cell disks

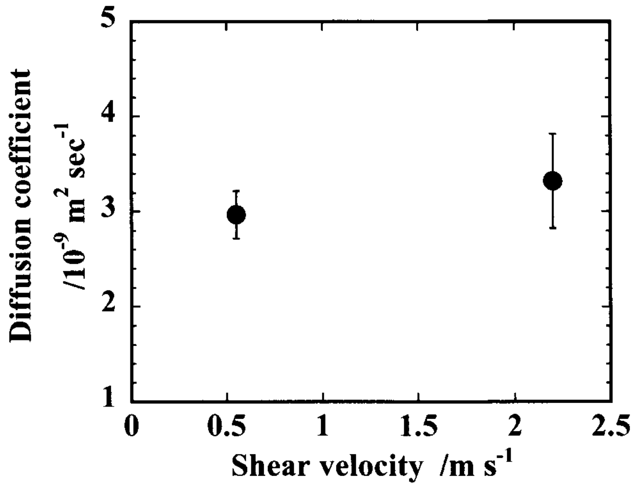


Fig.4 Effect of the shear velocity

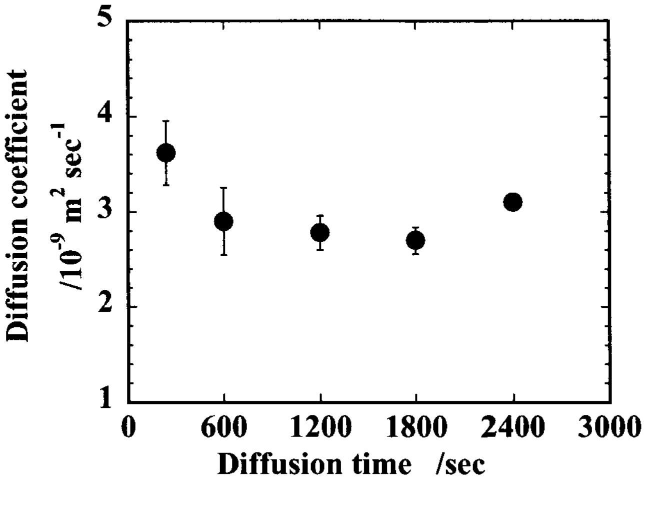


Fig.5 Effect of diffusion time

because of the buoyancy convection on the ground. On the other hand, the diffusion coefficient became also larger at the shorter diffusion time. The following can be considered. When the diffusion couple is formed, the mixing occurs due to the induced shear flow at the instant of joining and the initial concentration distribution is changed from the rectangular shape. It makes the obtained diffusion coefficient larger than the real value. This effect of initial mixing becomes smaller at longer diffusion time because the contribution of the change of the concentration distribution due to this induced flow becomes smaller at the longer time compared with that due to the true diffusion. It is concluded that there is an optimum diffusion time of shear cell experiments under gravity.

5. Conclusion

To find the optimum way to minimize the induced flow on joining, the effects of (1) surface roughness of the shear cell disks, (2) shear velocity and (3) diffusion period were investigated. It was found that (1) the shear cell disks should be rough (#100 emery paper finished), (2) the shear velocity should be low, and (3) there is the optimum diffusion time for the ground diffusion experiments.

Reference

1) M. Uchida, Y. Watanabe and T. Itami, International Symposium on experimental Methods for Microgravity Materials Science, June 2001 (Longbeach, U.S.A.)

2) M. Uchida, Y. Watanabe, S. Matsumoto, M. Kaneko, T. Fukazawa, T. Masaki and T. Itami, "The X-ray observation of the shear cell experiments for impurity diffusion of Au in liquid Ag", Journal of Non-Crystalline Solids 312-314 (2002) pp.203-207

3) M. Uchida, Y. Watanabe, M. Kaneko, T. Fukazawa and T. Masaki, "Development of shear cell with X-ray observation system", Modeling and Precise Experiments of Diffusion Phenomena in Melts under Microgravity Annual Report 2000 pp.107-111