InAs-GaAs interdiffusion measurements

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Interdiffusion coefficients of the InAs-GaAs system and self diffusion coefficients of InAs in the system InAs-^{113}InAs have been measured accuraely by using the sounding rocket TR-IA#7 and the shear cell method combined with glass sealing technique in microgravity. Measured diffusion coefficient were in the range between 1.2 to 4.1×10^{-8}m^2/s at temperatures between 1070 and 1200 ^{o}C. Two significant digits were obtained for regular compositional profile. In the measured temperature range, diffusion coefficients seemed to be dependent on T^5.

1. Introduction

$In_{1-x}Ga_xAs$ is a promising material for a substrate of laser diodes. Higher temperature stability of output power and emitting wavelength around 1.3 μm are expected by replacing InP substrate by $In_{0.3}Ga_{0.7}As$. For the growth of homogeneous $In_{0.3}Ga_{0.7}As$ single crystals, InAs-GaAs interdiffusion rate plays a key role, since it determines transport rate of solute in the melt and appropriate growth rate should be determined based on this transport rate. Required temperature gradient for avoiding constitutional supercooling is also dependent on the diffusion rate[1)]. If the diffusion rate is small, solute concentration variation at the solid-liquid interface becomes large and steep temperature gradient is required. However, InAs-GaAs interdiffusion coefficients have not been measured so far. The reason is difficulty in measurements: quenching of a InAs-GaAs melt does not fix the compositional profile in the melt because segregation occurs at solidification. Moreover, the system has high vapor pressure of As above melting temperature.

We measured InAs-GaAs interdiffusion coefficients precisely for the first time by using the shear cell method in microgravity, and by developing the glass sealing technique to confine As vapor in the cartridge. Compositional and temperature dependence of diffusion coefficients were measured by using diffusion couples with various In/Ga ratios in the temperature range between 1070 and 1200^{o}C. We also measured InAs self diffusion coefficients in the system InAs-^{113}InAs for comparing the magnitude of diffusion coefficients. Here, we report preliminary results of the experiment.

2. Experimental procedures

Diffusion experiments were performed at 1070, 1120 and 1200°C using a sounding rocket TR-IA #7. Five diffusion couples were used for each temperature as shown in Fig. 1. At each temperature, one couple is composed of InAs-^{113}InAs, which was used for measuring InAs self diffusion coefficient, and the rest were those for measuring InAs-GaAs interdiffusion coefficients. The shear cell technique was used[2]. Figure 2 shows the cross sectional view of the cartridge. The number of the cell is 16. Thickness of each cell is 1.5 mm and each cell has 5 holes with bore size of 1.5 mm. At each end, another cell with 19.5 mm thickness is placed. In this cell, carbon springs and plungers are inserted in each hole. They push the respective diffusion couple and give stress in the opposite direction for eliminating free melt surface when the melt is formed. In this cell, $InAs_{1.05}$ dummy samples are also placed for compensating As loss due to the reaction between As vapor and the cartridge material (Ta). The rod is rotated clockwise for connecting the diffusion couple after reaching experiment temperature and is rotated anti-clockwise for segmentation after appropriate diffusion period. We developed the glass sealing technique for confining As vapor in the cartridge[3] and at the support of the rod, the glass sealing technique is used.

The compositional profiles after diffusion experiments were measured by ICP (inductively coupled plasma) spectroscopy or by ICP mass spectroscopy. The estimated error in the measurements of In, Ga, or As concentration is within ±1%. Average diffusion coefficients were determined by finding a best fitted curve to the measured compositional profile on the basis of Fick's second law.

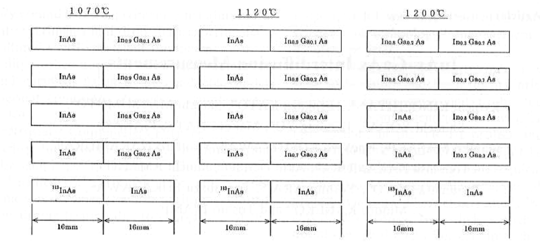


Fig. 1 Composition of diffusion couples.

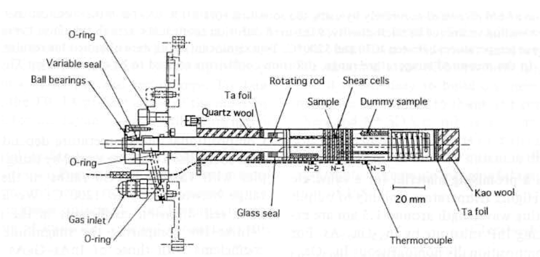


Fig. 2 Cross sectional view of the cartridge.

Diffusion coefficients can also be determined from the inclination of a straight line in the relation between inverse function of complementary error function and the distance as is given by the equation (1).

$$erfc^{-1}\left[2\frac{c_1 - c(x,t)}{c_1 - c_2}\right] = \frac{x}{2\sqrt{Dt}} \qquad (1)$$

where c(x, t) is concentration of a diffusion specie at distance x and at time t, c_1 ($x<0$) and c_2 ($x>0$) are initial concentration of diffusion specie. By using this relation, compositional dependence of diffusion coefficients was determined.

3. Results and discussion

The sounding rocket TR-IA #7 was launched on 19 November, 1998. Residual acceleration level was 10^{-4} G in microgravity conditions and no big disturbances were observed. Diffusion experiments were successfully terminated.

Diffusion period was 310 s for 1070°C, 278 s for 1120°C and 232 s for 1200°C, respectively. No leakage of melts from shear cell devices was observed and all cell holes were full of segmented and solidified materials. An example of 16 segments which compose of one diffusion couple are shown in Fig. 3. They show perfect cylindrical shapes and implying no free melt surfaces during diffusion experiments.

Temperature profile in the cartridge for the setting temperature of 1070°Cis shown in Fig. 4. Center thermocouple (N-1) was placed at the butting position of diffusion couples, and two side thermocouples (N-2 and N-3) were placed 18 mm away from the center thermocouple. Maximum temperature variations between these two thermocouples during experiments were 6.2°C. For 1120°C, it was 38.9°C and for 1200°C it was 12.5°C. Temperature variation in the devices reduces accuracy and precision in measurements and it should be kept minimum. Temperature uniformity in the device was the best for 1070°C and the worst for 1120°C.

Figure 5 shows an example of measured compositional profiles of In and Ga after diffusion experiment at 1070°C. Initial composition of the couple was InAs-$In_{0.9}Ga_{0.1}As$. Indium concentration was in the complementary relation to Ga concentration. Arsenic concentration was almost constant but several at.% of As was lost in spite of glass sealing of the cartridge and insertion of $InAs_{1.05}$ dummy sample in the cartridge, as is shown in Fig. 6. Arsenic loss was constant in the range between 4 at.% and 7 at.% and was not increased at 1200°C. Thus, the shear cell technique was applied without much arsenic loss at higher temperature of 1200°C. Since liquidus line does not coincide with solidus line in the InAs-GaAs system, we cannot fix the compositional profile in the melt even if the melt is quenched. Figure 7 is the example of the compositional profile obtained by quenching a uniform $In_{0.3}Ga_{0.7}As$ melt. Concentration becomes random by the segregation during quenching in such system. Therefore, the long capillary method usually used for diffusion measurements was not applicable to the InAs-GaAs system.

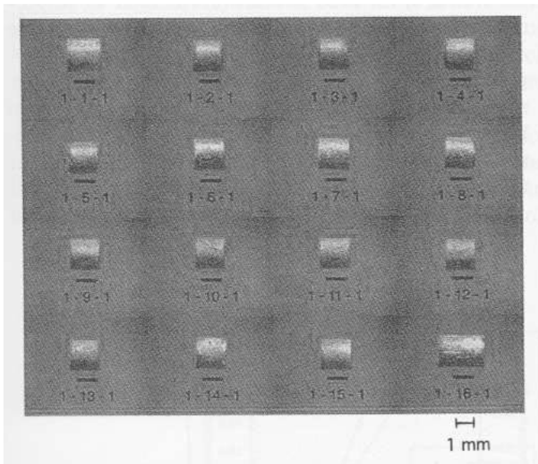


Fig. 3 An example of 16 segments which compose of one diffusion couple.

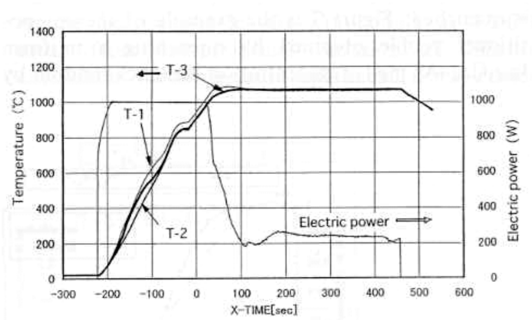
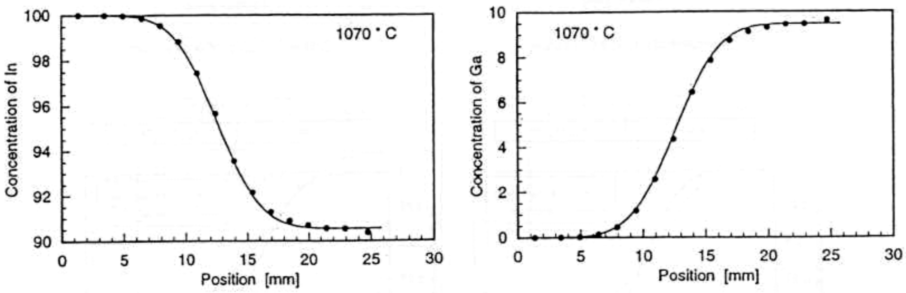


Fig. 4 Temperature profile in the cartridge for the setting temperature of 1070°C.

All measured concentration profiles of In and obtained diffusion coefficients are shown in Figs. 8 (a) for 1070°C, 8(b) for 1120°C and 8(c) for 1200°C, respectively. In Fig. 8(b), InAs was placed at the opposite side to the case of 1070 and 1200°C considering temperature variation in the furnace so that the higher melting temperature materials were placed at the higher temperature side.

Diffusion coefficients described in the figures are averaged values obtained from the best fitting method and solid curves are analytical concentration profiles calculated from the obtained diffusion coefficients. All diffusion couples at 1070°C show typical concentration profiles after diffusion and measured value lie on the analytical curves well but a few diffusion couples at 1120°C show random profiles and deviation of the measured values from the curves is noticed. At 1200°C, some segments near the composition of $In_{0.3}Ga_{0.7}As$ showed insufficient melting: the temperature in the cell might be between the solidus and liquidus because of high melting temperature of that composition. Therefore, the analytical curves are not extended to those points.



(a) Concentration profile of In (b) Concentration profile of Ga

Fig. 5 Measured compositional profiles of In and Ga after diffusion experiment at 1070°C.

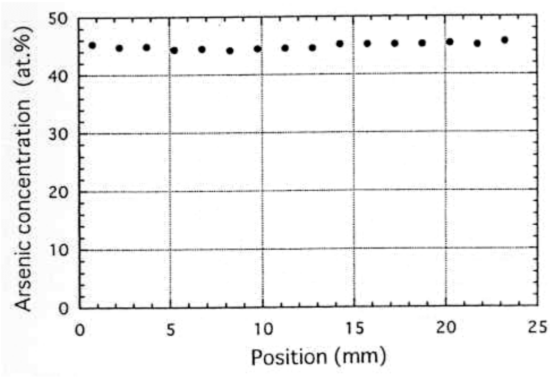


Fig. 6 Arsenic concentration in the sample after diffusion experiment.

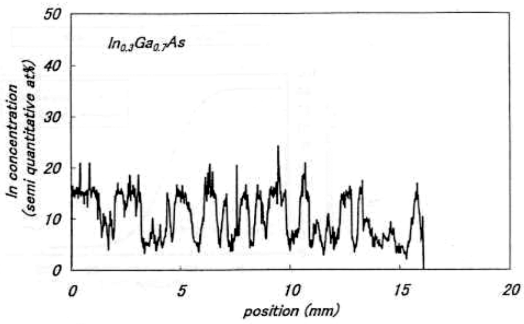


Fig. 7 Compositional profile obtained by quenching a uniform $In_{0.3}Ga_{0.7}As$ melt.

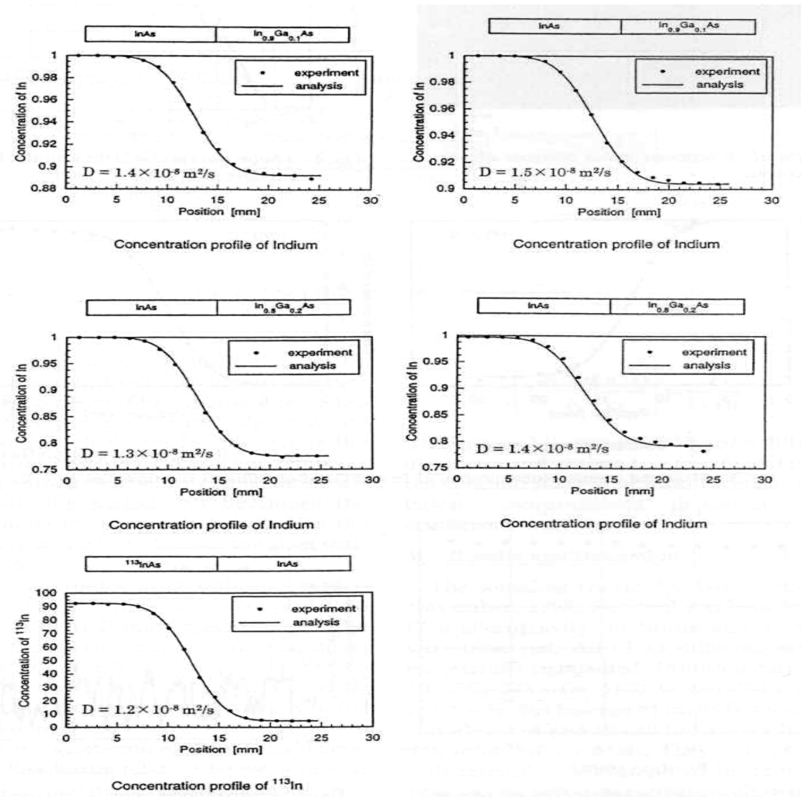


Fig. 8(a) Measured concentration profiles of In for 1070℃.

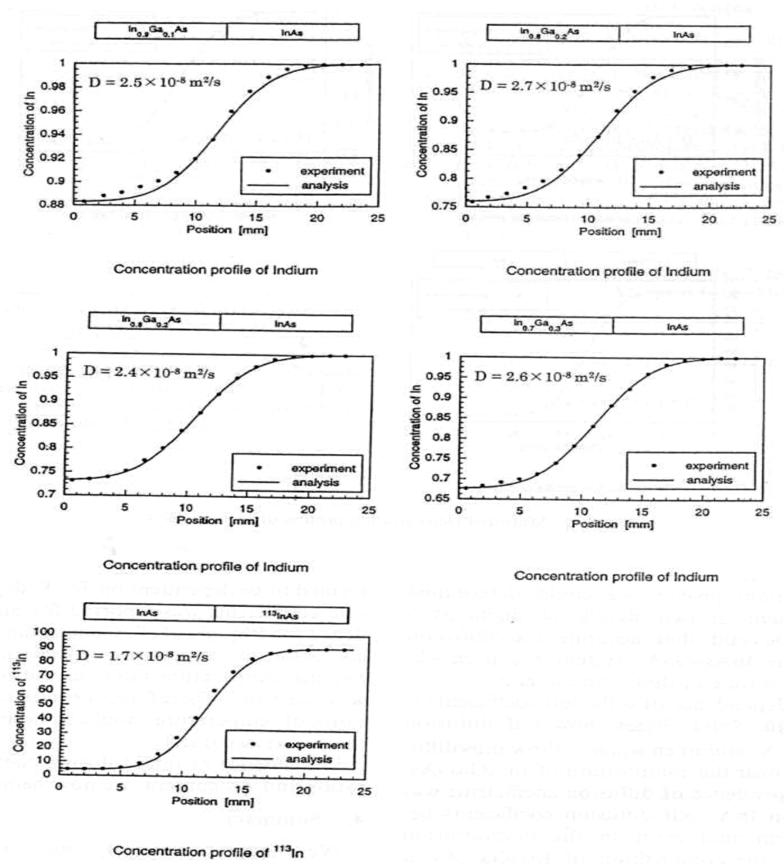


Fig. 8(b) Measured concentration profiles of In for 1120℃.

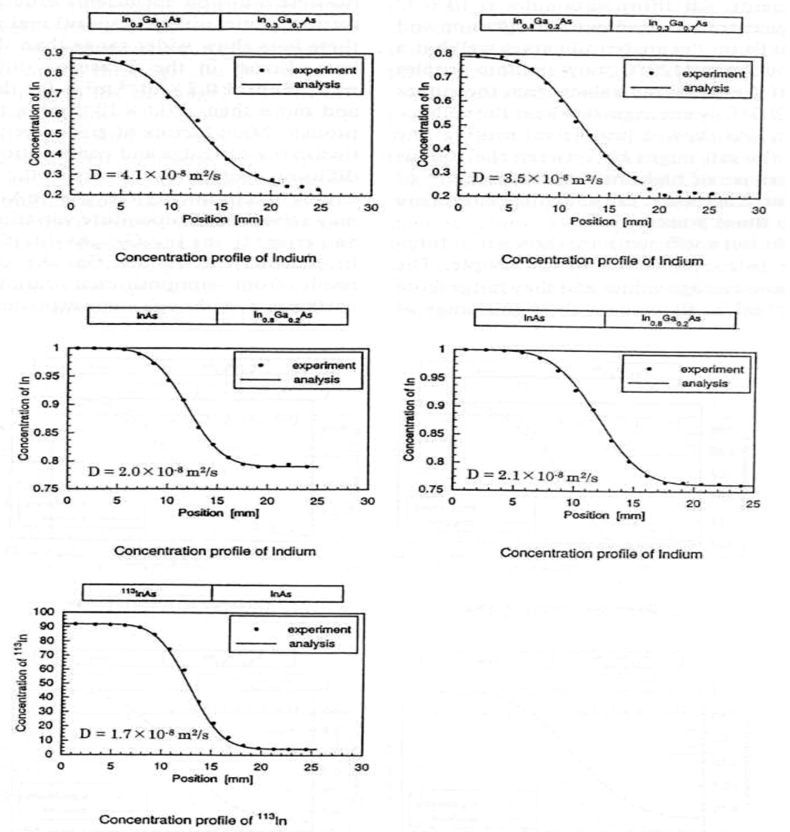


Fig. 8(c) Measured concentration profiles of In for 1200℃.

In Fig. 9, diffusion coefficients are shown as a function of average In concentration of the couple. The center marks show average values and they rage from 1.2 to $4.1\times10^{-8}m^2/s$. Error bars show the range of possible diffusion coefficients estimated from the distortion of measured compositional profiles. Note that these bars show wider range than the statistical error bars. Errors in the measured diffusion coefficients were about $\pm0.2\times10^{-8}m^2/s$ for the ordered profiles and more than $\pm0.6\times10^{-8}m^2/s$ for the disordered profiles. Main factors of errors are temperature variation in the cartridge and compositional dependence of diffusion coefficients. Errors in the $In_{0.9}Ga_{0.1}As$-InAs couple and in the $In_{0.8}Ga_{0.2}As$-InAs couple at 1120℃ may arise from temperature variation in the cartridge and errors in the $In_{0.9}Ga_{0.1}As$-$In_{0.3}Ga_{0.7}As$ couple and in the $In_{0.8}Ga_{0.2}As$-$In_{0.3}Ga_{0.7}As$ at 1200℃ result from compositional variations of diffusion coefficients. Although some experiments showed disordered compositional profile, we could determined diffusion coefficient in two significant digits as a whole. It can be said that accurate interdiffusion coefficients in the InAs-GaAs system has been obtained for the first time in these experiments.

Temperature dependence of diffusion coefficients is shown in Fig. 10. Solid circles show self diffusion coefficients of InAs and open squares show inerdiffusion coefficients near the composition of $In_{0.8}Ga_{0.2}As$. Temperature dependence of diffusion coefficients was derived based on InAs self diffusion coefficients because the experimental error in the interdiffusion coefficients near the composition of $In_{0.8}Ga_{0.2}As$

at 1120°C was great. The obtained temperature variation seemed to be dependent on T^5. T^2 dependence of diffusion coefficients was reported for Sn[4] and $T^{2.4}$ dependence for $Pb_{1-x}Sn_xTe$[5]. Comparing with these materials, obtained temperature dependence was rather great but the temperature range in the present experiment was narrow. Therefore, experiments in the wider range of temperature should be necessary to determine the power accurately. Dependence of interdiffusion coefficients on In/Ga ratios and As content are now being analyzed.

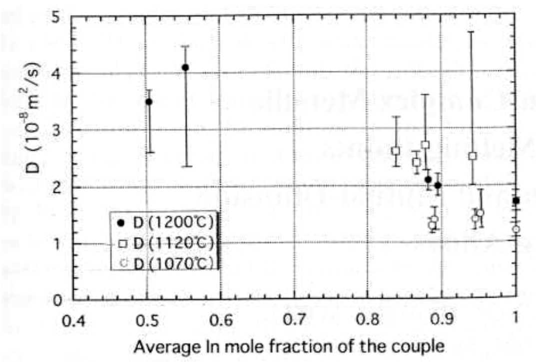


Fig. 9 Diffusion coefficients as a function of average In concentration of the couple.

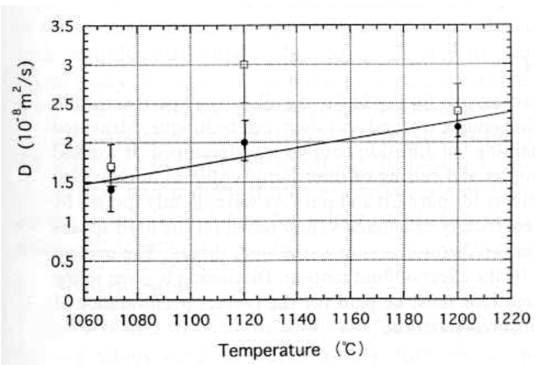


Fig. 10 Temperature dependence of diffusion coefficients.

4. Summary

We have successfully measured interdiffusion coefficients in the InAs-GaAs system and self diffusion coefficients of InAs in the system of InAs-^{113}InAs by using the sounding rocket TR-IA#7. Segregation and high As vapor pressure made the measurements difficult, but we have succeeded in determining diffusion coefficients accurately for the first time in these systems by adopting the shear cell method combined with glass sealing technique. Measured diffusion coefficients were in the range between 1.2 to $4.1 \times 10^{-8} m^2/s$ at temperatures between 1070 and 1200 ℃. Error in measurements were analyzed and main factors are found to be temperature variation in the cartridge and compositional dependence of interdiffusion coefficients. Temperature dependence of diffusion coefficients seems to be proportional to T^5 judging from the data.

References

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