In-Situ Observation of Composition Profiles in the Solution by X-ray Penetration Method

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Abstract

The X-ray penetration intensity during the diffusion process of NH_4Br into H_2O was measured by a CdTe line sensor as a function of time and it was converted to the NH_4Br composition using a calibration line. The diffusion coefficient of NH_4Br into H_2O was estimated to be 2.2 x 10^{-5} cm^2/s by comparing the calculated results. The method was applied to the growth of InGaSb from the In-Ga-Sb solution. The indium composition profiles in the solution were measured and growth of InGaSb from the In-Ga-Sb solution was observed from change of X-ray intensity. The growth region of InGaSb crystal was confirmed by the electron probe micro analysis. It was demonstrated that the X-ray penetration method was a powerful method to measure the composition profiles in the solution.

1. Introduction

Ternary alloy semiconductor crystals are important materials for opto-electronic devices because fundamental properties such as lattice constant and band gap can be controlled by adjusting composition ratio. The alloy crystals offer the possibility to reduce the problem of lattice mismatch at the interface between a substrate and an epilayer. Ternary alloy crystals such as InGaAs [1-7], InGaSb [8-12], InSbBi [13-14], InAsSb [15-16] have been grown until now. However, it is very difficult to grow large single crystals of high quality, because there are three major problems which must be overcome. The first is the constitutional supercooling which brings about the instability at the growth interface [17]. The second is the change of composition profiles both in the crystal and in the solution during growth. Since the segregation coefficient of each component is not unity, the composition ratio in the

alloy crystal continues to change. The third relates to the flows caused by heat and mass transfer. The quality of alloy crystals is strongly affected by the flow patterns.

We have grown homogeneous InGaSb crystals by the temperature cooling method under a constant temperature gradient using a GaSb(seed)/Te-doped InSb/GaSb(feed) sandwich structure [18]. At 600°C, an InSb crystal is completely melted since the melting temperature of InSb is 525°C. GaSb seed crystal and GaSb feed crystal partially dissolve into In-Sb melt and In-Ga-Sb solution is formed. The temperature at solution/feed interface is higher than that seed/solution interface, which results GaSb composition at solution/feed interface higher than that of seed/solution interface. Therefore, the GaSb moves to the seed/solution interface by diffusion and convection due to GaSb composition gradient between solution/feed and seed/solution interface. The solution near the seed/solution interface becomes supersaturated, which cause spontaneous $In_xGa_{1-x}Sb$ crystal growth at seed/solution interface without moving the ampoule. Since the segregation coefficient of GaSb is larger than unity, the larger amount of GaSb component is incorporated in the $In_xGa_{1-x}Sb$ crystal. As a result, GaSb component in the solution is deficient during growth. GaSb component should be supplied during growth to grow homogeneous $In_xGa_{1-x}Sb$. To grow homogeneous crystals, the balance among the dissolution rate of feed, growth rate of crystal and the transportation of solute in the solution is very important. Since the degree of constitutional supercooling also relates to the composition profile in the solution, the development of the in-situ measurement technique of the composition profile in the solution during growth is strongly required.

Interferometry technique using a laser is a very useful method to investigate the composition profile near the growth interface in the solution [19-20]. However, it is

very difficult to measure the composition profile in the metallic solution since the light can not penetrate into it. On the other hand, Kakimoto et al. measured solid-liquid interface shape by X-ray radiography method during crystal growth of Si since X-ray can penetrate into Si melt [21].

We have developed the X-ray penetration method using a CdTe line sensor to investigate the composition profile in the solution. At first, the diffusion experiment of NH_4Br into H_2O was carried out to investigate the validity of the X-ray penetration method. The composition profile was detected as a function of time and the profile was compared with the calculated profile. Since the both results agreed well, the X-ray penetration method was adapted to investigate the composition profile in the In-Ga-Sb solution during growth.

2. Experimental method

Fig. 1 shows a configuration of the measurement system. The sample was set up on the platform, which could move along X, Y and Z axis and could rotate 360 degree. X-ray source is a tungsten target with an acceleration voltage of 150 kV. The detector is a CdTe line sensor composed of 64 segments. The shape of a segment is rectangle, and the width is 2 mm and the height is 1 mm. So, total height of the sensor is 64 mm. The diffusion process of NH_4Br into H_2O was in-situ measured at 20°C by the X-ray penetration method with an X-ray current of 31 µA. In order to get a relationship between the X-ray penetration intensity and the NH_4Br composition in H_2O, nine samples with different NH_4Br composition of 0, 5, 10, 15, 20, 25, 30, 35, 40 wt% were prepared. The X-ray penetration intensity of the samples was transformed into absorbance and the calibration line between absorbance and NH_4Br composition

was fabricated.

Fig. 2 shows the configuration of the sample. Initially, NH_4Br solution with 40 wt.% composition and H_2O were separately inserted into the glass boxes. The lengths of the NH_4Br solution and H_2O were 1 cm and 1 cm, respectively. They were divided into two parts by a sheet to establish initial condition. Since the density of NH_4Br is 2.429 g/cm^3 and it is larger than that of H_2O, NH_4Br solution was set under H_2O. In order to make clear the position of the sample, lead (Pb) plates were placed at the top and the bottom area of the sample. Since the X-ray did not penetrate the Pb plate, the edge of the sample was distinguished. The mixing of the solution was started by removing the sheet. After 3 min, the X-ray penetration intensity was measured continuously as a function of time and it was converted to the NH_4Br composition using the calibration line. The absorbance values of the Pb plate and air were divided into 1275 scales and displayed in color. The composition profiles were calculated by solving the diffusion equations by finite difference method and compared with the experimental results.

This method was applied to measure the profile of indium composition in the In-Ga-Sb solution during growth of InGaSb on a GaSb seed. Fig. 3 shows the configuration of the sample and the temperature profile. GaSb and InSb crystals were processed into cylindrical shape and the GaSb(seed) - InSb - GaSb(feed) sandwich sample was prepared. The respective lengths of the GaSb and InSb were 0.8 cm and 0.4 cm. The GaSb/InSb/GaSb sandwich sample with the diameter of 2 mm was taken in a BN tube, and then inserted into a quartz tube. It was evacuated to about 10^{-4} Pa and sealed. We have measured the temperature gradient in the furnace by using the thermocouples before experiment, but could not measure the temperature gradient in

the sample since the sample was inserted in the quartz. The temperature gradient of the furnace was 1.3°C/mm. The temperature was monitored by the thermocouple positioned outside the ampoule.

The sample was vertically set up in the furnace. The X-ray penetration intensity of the sample was measured by moving the sample along the Y axis. Since the sample was cylindrical, the X ray penetration intensity from the center of the sample had the smallest value. We fixed the sample at the place where the X-ray intensity was the smallest. The X-ray image of the sample was displayed on the screen. So, we could check the sample was inclined or not. The distance between the X-ray source and sensor was also adjusted to match the sample shadow by moving the sensor to the X direction. The distance between the X ray source and the sample was 320 mm and that between the X ray source and the sensor was 952mm. The image of the sample was magnified about 3 times on the sensor. Since the size of a segment of the sensor was 1 mm, the resolution of the sensor was about 0.33 mm.

The acceleration voltage was 150 kV and current was 1 mA. In order to get a relationship between the X-ray penetration intensity and $In_xGa_{1-x}Sb$ composition, the X-ray penetration intensities of GaSb and InSb solids were measured. They were transformed into absorbance. The calibration line between absorbance and $In_xGa_{1-x}Sb$ composition was determined.

The temperature of the furnace increased to 600°C and then kept constant. After that, the sample was loaded into the furnace. The InSb crystal was completely melted and 2 solid-liquid interfaces were established. The X-ray intensity of the sample was measured as a function of time. The measurement was carried out for 5 h by keeping the reference temperature constant. After that, the sample was quenched by

turning off the power of the heater.

After the X-ray penetration experiment, the sample was cut parallel to the growth axis and the surface was polished with an abrasive of 5 μm. The indium composition profile was measured by the Electron probe micro analysis (EPMA). The EPMA measurement was carried out at every 10μm near the growth area.

3. Result and discussion

3.1 NH_4Br composition profiles in H_2O

Fig. 4 shows the NH_4Br composition profiles as a function of time. The composition profiles were displayed with color scale. The measurement was carried out every 0.2 sec and the one figure includes the data of 1 min. The red color indicates that the X-ray intensity could not be measured due to a flaw of CdTe cell. The black area and green area at the top and bottom region indicates the positions of Pb plate and quartz box, respectively. Pb plates were fixed on the top and bottom of the quartz box using an adhesive tape. The X ray penetration intensity of the adhesive tapes was stronger than that of the quartz. Therefore, the area of adhesive tapes appears yellowish color between Pb and quartz. The yellow and blue color indicates H_2O and NH_4Br solution, respectively. The green color between the yellow and blue shows the mixing of H_2O and NH_4Br solution. As the time was passed, the green area increased. It indicated that diffusion of NH_4Br into H_2O was proceeded.

Fig. 5 shows the NH_4Br composition profiles as a function of time. The X axis indicates the distance from the bottom of 40 % NH_4Br solution. The initial position of the NH_4Br solution and H_2O was located at 1 cm. Open triangles, closed triangles, open circles and closed circles indicate the profiles at 3, 20, 40 and 60 min

after the measurement, respectively. It is clearly shown that NH_4Br composition was gradually decreased from the left side to the right side with time.

The composition profiles were calculated by solving the diffusion equations using finite difference method. The composition profile was calculated by assuming the value of the diffusion coefficient and compared with the experimental results. The procedure was repeated by changing the diffusion coefficient till the calculated profile fit the experimental result. Fig. 6 shows the profiles at 60min. A dotted line, a solid line and a broken line indicate the profiles calculated using the diffusion coefficient of 1.6 x 10^{-5} cm^2/s, 2.2 x 10^{-5} cm^2/s and 3.0 x 10^{-5} cm^2/s, respectively. The diffusion coefficient of NH_4Br solution into H_2O was estimated to be 2.2 x 10^{-5} cm^2/s. There is a small discrepancy between the experimental result and the calculated result. Capillary effect and convection due to the opening of the gate may affect the composition profile.

3.2 Indium composition profiles of the GaSb/InSb/GaSb sandwich sample

Fig. 7 indicates the indium composition profiles of the GaSb/InSb/GaSb sandwich sample measured by X-ray penetration method. The circular, rectangular and triangular points show the indium composition profiles at 1, 3 and 5 h after loading the sample in the furnace, respectively. The GaSb seed and feed crystals were placed between the distance from 0 to 0.8 cm and from 1.2 cm to 1.8 cm, and the InSb was placed from 0.8 cm to 1.2 cm at the initial stage. Since the melting temperature of InSb was 525˚C, an InSb crystal was completely melted at 600˚C. Since the respective densities of liquid InSb and solid InSb were 6320 kg/m^3 and 5780 kg/ m^3, the volume of the InSb decreased about 9 % by changing from solid to liquid. Since the GaSb feed was partially dissolved in the InSb melt, the position of the GaSb feed was shifted from

1.2 cm to 1.1 cm. The length of the GaSb seed was also decreased from 0.8 cm to 0.64 cm by dissolving into the InSb melt. The indium composition ranged from 0.4 to 0.6 at the middle region between the GaSb seed and In-Ga-Sb solution. The region corresponded to the InGaSb crystal grown on the GaSb seed. The value of the indium composition in the In-Ga-Sb solution near the InGaSb crystal was larger than that near the GaSb feed. It was because the temperature of the GaSb feed was higher than that of the GaSb seed. Since larger amount of GaSb feed could dissolve into the solution, the indium composition decreased. The indium composition in the solution was increased as the time passed from 1 h to 5 h. It was because the segregation coefficient of indium is less than unity. Since the indium composition in the crystal was smaller than that of the solution, the indium was accumulated in the solution with time.

The indium composition profile measured by EPMA after the X-ray penetration experiment was shown in fig. 8. It was found that InGaSb crystal was grown near the GaSb seed and the value of the indium composition was about 0.3. It corresponded to the solidified temperature of about 588˚C. The Indium composition gradually increased from 0.3 to 0.9. It indicated the InGaSb was grown by decreasing the temperature and finally residual solution with the high indium composition was solidified. The indium composition measured by the X-ray penetration method ranged from 0.4 to 0.6 at the distance between 0.65 cm and 0.7 cm as shown in Fig.7. The date points were only 2 points. It was because the resolution of the sensor was about 0.33mm. We estimated the region to be InGaSb grown area by comparing the profile measured by EPMA.

4. Conclusion

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Diffusion process of NH_4Br into H_2O was in-situ measured by the X-ray penetration method using a CdTe line sensor. A calibration line was established by measuring the relationship between the X-ray penetration intensity and the NH_4Br composition in H_2O. The diffusion coefficient of NH_4Br into H_2O was estimated to be 2.2×10^{-5} cm^2/s by comparing the calculated composition profiles with the experimental results. The method was applied to the growth of InGaSb from the In-Ga-Sb solution. The GaSb/InSb/GaSb sandwich sample with the diameter of 2mm was heated to 600°C under a temperature gradient of 1.3°C/mm. The Indium composition profiles in the solution and of the InGaSb grown crystal were measured as a function of time. The growth region of InGaSb crystal was confirmed by the electron probe micro analysis. It was demonstrated that the X-ray penetration method was a powerful method to measure the composition profiles in the solution.

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Figure captions

Fig. 1. Configuration of the measurement system. X-ray source with a tungsten target with an applied voltage of 150kV and a CdTe line sensor were used.

Fig. 2. Configuration of the sample. Initially, NH_4Br solution and H_2O were separately inserted into the glass boxes. The mixing of the solution was started by removing a sheet between NH_4Br solution and H_2O.

Fig. 3. Configuration of the sample. (a) temperature profile, (b) ampoule configuration and (c) outside view of the ampoule.

Fig. 4. NH_4Br composition profiles as a function of time. The composition profiles were displayed with color scale. The x-axis indicates the time lapse.

Fig. 5. NH_4Br concentration profiles as a function of time. The x axis indicates the distance from the bottom of 40% NH_4Br solution.

Fig. 6. The solid circles indicate the experimental data at 60 min. A dotted line, a solid line and a broken line indicate the profiles calculated using the diffusion coefficient of $1.6 \times 10^{-5}\,cm^2/s$, $2.2 \times 10^{-5}\,cm^2/s$ and $3.0 \times 10^{-5}\,cm^2/s$, respectively.

Fig. 7. Indium composition profiles of the GaSb/InSb/GaSb sandwich sample measured by X-ray penetration method. The circular, rectangular and triangular points indicate the indium composition profiles at 1 h, 3 h and 5 h after loading the sample, respectively.

Fig. 8. The indium composition profile measured by EPMA after the X-ray penetration

experiment.