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Growth of $In_xGa_{1-x}Sb$ Bulk Crystals by Czochralski Technique

To grow InGaSb with larger In composition, step growth process was adapted. By increasing the In composition step by step, $In_{0.1}Ga_{0.9}Sb$ single crystal of length 18mm was grown. Intensities and the FWHM values of X-ray diffraction spectrum were, respectively, 10 times larger and one third of the value, compared with the values of the crystal grown directly from GaSb seed crystal.

Keywords: *Crystal growth, InGaAs crystal, step growth, GaSb seeding*

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1. Introduction

Dyring the last few years much attention has been directed to grow ternary semiconductor bulk crystals with uniform composition. Since the lattice constant can be controlled by adjusting compositional ratio, these crystals offer the possibility to reduce the problem of lattice mismatch caused at the interface between a substrate and an epilayer. Ternary semiconductors such as InGaAs [1-2], GaAsP [3], InSbBi [4] and InGaSb [5-7] have been grown at present. However, it is very difficult to grow large ternary single crystals of high quality, because there are three major problems, which must be overcome. The first is the constitutional supercooling near the growth interface in the solution. If the degree of the constitutional supercooling is large, unstable growth gets generated, and subsequently polycrystals result. The second is the compositional change in the solution during growth. Since the segregation coefficient of each component is not unity, the compositional ratio in the crystal continues to change during growth. The third is the difference of lattice constants between the seed and the grown crystal. It brings about strain in the crystal, and consequently, many dislocations are introduced.

To reduce the degree of constitutional supercooling, we have developed two new methods. One of them is the Czochralski method modified so as to introduce ultrasonic vibrations (10kHz) into the melt from the crucible bottom [8-11]. By increasing the output power of ultrasonic vibrations, $In_xGa_{1-x}Sb$ single crystal with higher In compositional ratio ($0<x<0.15$) were grown. The other method is a modified Bridgman method [12-15]. A relative motion between the growing surface and the solution can be given by rotating the growth ampoule at high speeds under covering about 60 to 90% of the growing surface with the solution.

To reduce the difference of lattice constants between GaSb seed and InGaSb grown crystal, a step growth process is adopted and the results are reported in this paper. First, $In_xGa_{1-x}Sb$ ($x=0.03$) single crystal was grown from a GaSb seed, and it was used as a seed to grow $In_{0.05}Ga_{0.95}Sb$. This process was continued to grow $In_{0.1}Ga_{0.9}Sb$. The quality of the grown crystal was compared with that of the $In_{0.1}Ga_{0.9}Sb$ crystal grown directly from GaSb seed.

2. Experiment

Figure (1) shows a schematic representation of an apparatus for Czochralski technique. A double crucible made of carbon was used to eliminate oxides from the melt surface. The outer crucible was 130mm in height, and the size of the inner crucible was 30mm in ID and 30mm in depth. A small hole was made at the bottom of the inner crucible. When the InGaSb charged material was molten, the inner crucible was pulled down by a weight hung from its edge. The melt flowed up through this small hole and the oxide slag was eliminated from the melt surface. A 25kHz rf power generator was employed to heat the crucibles which were kept in hydrogen atmosphere with hydrogen gas was flowing at a rate of 300cm^3/min. The ratio of InSb to GaSb used as source materials for growing $In_xGa_{1-x}Sb$ crystals was decided using InSb-GaSb binary phase diagram [16]. At first, a GaSb single crystal was used as a seed and $In_xGa_{1-x}Sb$

(x=0.03) was pulled in the <111> direction. The crystal rotation rate was fixed at 10rpm and the pulling speed was changed between 2.5mm/h and 5mm/h during the seeding and growth processes. By cutting the crystal 30mm from its bottom, $In_xGa_{1-x}Sb$ (x=0.03) seed crystal was obtained. $In_xGa_{1-x}Sb$ (x=0.05) single crystal was grown from $In_xGa_{1-x}Sb$ (x=0.03) seed. By repeating this process, $In_xGa_{1-x}Sb$ (x=0.1) was grown. This process is referred as step growth process. An $In_xGa_{1-x}Sb$ (x=0.1) crystal was grown directly from a GaSb seed (it is referred as direct growth process), and the quality of the crystal was compared with that of the crystal grown by step growth.

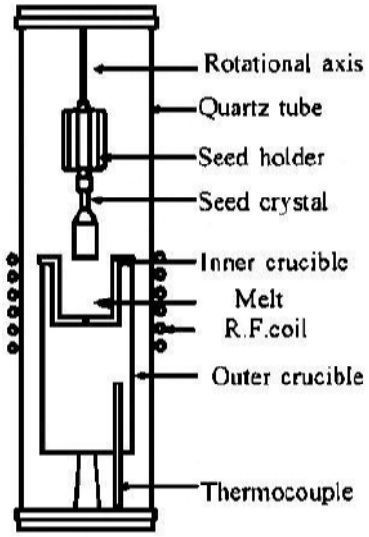

Fig. (1): Schematic representation of a Czochralski growth apparatus

Pulled crystals were cut along the growth direction so as to expose a (110) plane. Their cut surface were sufficiently polished with a 5μm-diameter alumina abrasive, and surface morphologies were observed. Electron probe microanalysis (EPMA) was done to study the compositional profiles. To measure the quality of the crystal, the X-ray intensity profile with respect to 2θ was measured using a four-crystal X-ray diffractometer.

3. Results and Discussion

At first, an $In_{0.03}Ga_{0.97}Sb$ single crystal was grown from a GaSb seed to make an $In_{0.03}Ga_{0.97}Sb$ seed. Figure (2) shows an outside view of an $In_{0.03}Ga_{0.97}Sb$ single crystal grown from a GaSb seed crystal. To prevent the dislocations from propagating into the crystal from seed necking procedure was carried out. This involved gradually reduction of diameter of the crystal until a long neck was grown. The crystal diameter was then increased to the desired size and then maintained constant. The diameter and the length of the crystal were 9mm and 73mm, respectively. By cutting the crystal 30mm from the bottom, $In_xGa_{1-x}Sb$ (x=0.03) seed crystal was constructed.

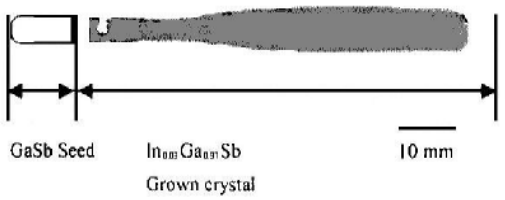

Fig. (2): Outside view of GaSb seed crystal and $In_{0.03}Ga_{0.97}Sb$ grown crystal

Figure (3) shows a (110) cut surface of an $In_xGa_{1-x}Sb$ crystal and the indium compositional profile measured along the pulling direction by EPMA. From the $In_{0.03}Ga_{0.97}Sb$ seed, $In_xGa_{1-x}Sb$ (x=0.05, 0.07, 0.09, 0.1) single crystal was grown step by step. Although the tip of the $In_{0.1}Ga_{0.9}Sb$ was polycrystalline, single crystal with the length of about 18mm was grown. The In composition was uniform in each region and its value changed step by step. This indicates that the step growth was effective to increase the In composition.

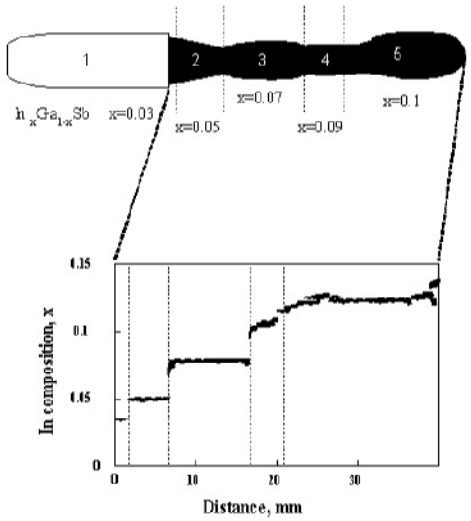

Fig. (3): (110) cut surface of an $In_xGa_{1-x}Sb$ crystal and the indium compositional profile measured along the pulling direction by EPMA

The X-ray intensity profile with respect to 2θ measured in different regions (1~5) in Figure (3) was shown in Figure (4). The diffraction angle shifted towards lower angle by increasing the In compositions. From the values of 2θ, the lattice constants were calculated by using Bragg equation. Then the value of the In composition was calculated using Vegard's law. As a result, In composition of 1, 2, 3, 4, 5 regions were calculated as 0.028, 0.052, 0.069, 0.087 and 0.098, respectively. These values coincided with those obtained from EPMA measurements.

Figure (5) shows the X-ray diffraction spectra of the $In_xGa_{1-x}Sb$ (x=0.1) single crystal grown by step growth process and direct growth process. The values of 2θ at the peaks were 41.61° in both the crystals. However, the intensity and the FWHM were quite different. Intensities of X-ray diffraction spectra and the FWHM values of the crystal grown by step growth process were, respectively, 10 times larger and one third of the value, compared with the values of the crystal grown directly form GaSb. Misfit may be considered as the reason for this. The misfit between GaSb and the $In_xGa_{1-x}Sb$ (x=0.1) was 0.63%. On the contrary, the misfit between the $In_xGa_{1-x}Sb$ (x=0.1) and $In_xGa_{1-x}Sb$ (x=0.09) was 0.063% which is 10 times smaller than that of direct growth. These results clearly indicated that the step growth was very effective to improve the quality of InGaSb ternary crystals.

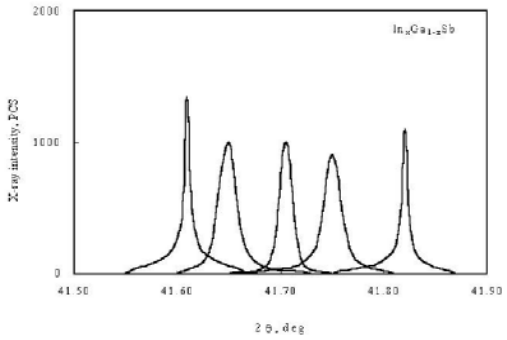

Fig. (4): The X-ray intensity profile with respect to 2 θ measured in the regions (1-5) in Figure (3)

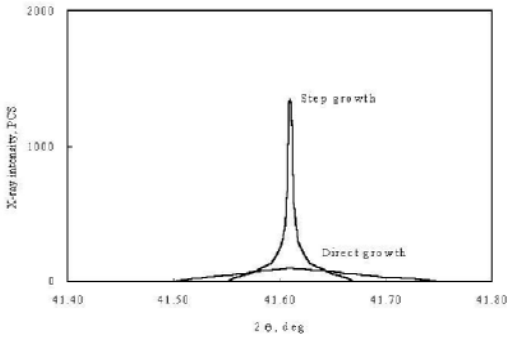

Fig. (5): The X-ray diffraction spectra of the $In_xGa_{1-x}Sb$ (x=0.1) single crystal grown by step growth process and direct growth process

4. Conclusions

A step growth process was adopted to grow $In_xGa_{1-x}Sb$ (x=0.1). By increasing the In composition step by step, $In_{0.1}Ga_{0.9}Sb$ single crystal of length 18mm was grown. To compare the quality of the crystal grown by step growth, an $In_xGa_{1-x}Sb$ (x=0.1) crystal was grown directly from a GaSb seed. Intensities and FWHM values of X-ray diffraction spectrum of the crystal grown by step growth process were, respectively, 10 times the values of the crystal grown directly from GaSb.

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