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LPE Growth of $(3GaAs)_x\{(3ZnSe)_y(Ga_2Se_3)_{1-y}\}_{1-x}$ Alloy

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1. Introduction

ZnSe, Ga_2Se_3 and GaAs have a zincblende structure and a direct band gap of which value is 2.67, 1.92 [1] and 1.42eV, respectively. Therefore, using the alloy system among them, light emitting devices covering almost all of the visual spectrum range could be realized. Especially, the development in growth technique of ZnSe-GaAs alloy makes it possible to fabricate the hetero-junction devices on either substrate of ZnSe or GaAs under the near lattice-matching condition.

Previously we reported that the quasi-ternary alloy layers represented by $(3GaAs)_x\{(3ZnSe)_y(Ga_2Se_3)_{1-y}\}_{1-x}$ could be grown on a ZnSe (100) substrate from Ga solvent in a closed quartz tube [2]. The alloy composition y was nearly equal to 0.8 , not sensitive to the growth temperature and cooling rate.

In this study, we investigate the behaviours of Zn-Ga-As-Se system to control the alloy composition.

2. Experiment

The growth experiments were carried out using a carbon slide boat placed in an evacuated quartz ampoule. ZnSe (100) substrates used were prepared by the physical vapor deposition method [3]. Pure Ga or Zn added Ga was used as a solvent. Source materials were a GaAs platelet and a ZnSe polycrystalline ingot. A small amount of Se was sealed occasionally in the ampoule to apply vapor pressure. The ampoule was set in a tipping furnace, and the temperature was raised to 900 ℃ and held for 4 hours to establish a complete saturation. Then the substrate was contacted to the solution by tipping the furnace, and cooled down. At the end of the growth, the substrate was removed from the solution by counter tipping of the furnace. Typical growth conditions were listed in Table I.

Samples were cleaved and the composition profile in the grown layer was measured by electron probe micro-analysis (EPMA). Lattice constants were determined by X-ray diffraction. Photoluminescence spectra were measured at room temperature under the excitation of a He-Cd (325 nm) laser.

Table I Conditions of Crystal Growth

Sample Number	#1	#2	#3
Solvent	Ga	Ga+Zn	Ga (under Se vapor pressure)
Contact Temp.	900℃	900℃	900℃
Remove Temp.	860℃	r.t.	860℃
Cooling Rate	0.2℃/min	2℃/min	0.2℃/min

3. Results and discussion

Alloy layers grew on a ZnSe substrate with a uniform thickness. The thickness was about 120 μm for the GaAs-rich samples, and decreased according as the ZnSe content increased. X-ray diffraction measurements conformed the epitaxial growth of the layers on ZnSe substrates. EPMA measurements in a cross section revealed the distribution of Zn, Ga, As and Se along the growth direction. By applying the representation of the quasi-ternary alloy $(3GaAs)_x\{(3ZnSe)_y(Ga_2Se_3)_{1-y}\}_{1-x}$, the alloy compositions, x and y , were calculated in each sample.

For the sample #1 grown from pure Ga solvent, the alloy composition y was maintained at 0.8 during the growth, while the composition x increased from 0.6 to 0.9 as the layer grew. For the sample #2 grown from the

Ga+Zn solution, the composition y was kept at 1, meaning that a pseudo-binary alloy of (GaAs)x(ZnSe)1-x was obtained, although the alloy composition was limited in a GaAs-rich region (x>0.85). For the sample #3 grown under Se vapor pressure of 6×10^4 Pa, x value increases from 0.25 to 0.5 along the growth direction, while y value was kept at 0.4.

From the results mentioned above, it can be said that the addition of Zn into Ga solution is effective to suppress the generation of Ga_2Se_3 component, and supply of Se vapor pressure gives a contrary effect. Thus, selecting the growth condition, the alloy composition can be controlled.

Fig.1 gives the triangle representation of the quasi-ternary alloy obtained in this series of experiments, in which thick arrows show the growth direction and the composition range.

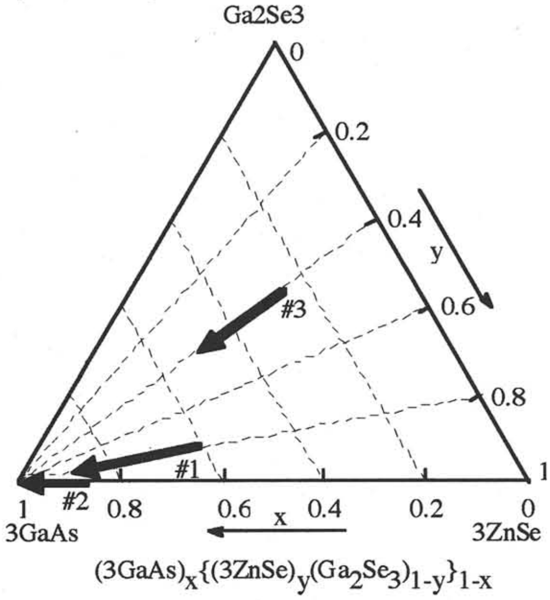

Fig.1 Triangle representation of the alloy composition

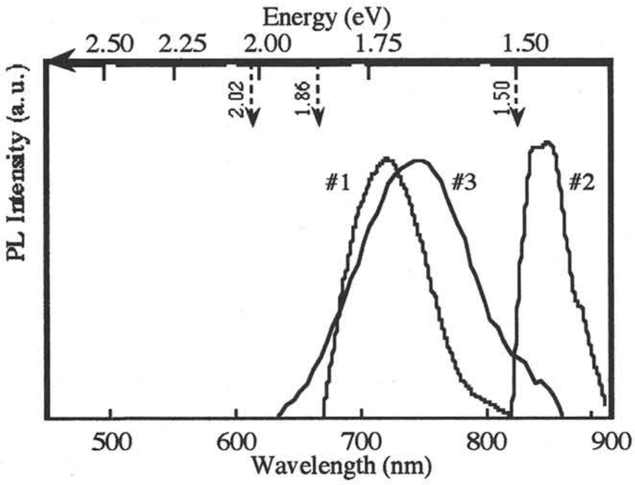

Fig.2 Photoluminescence spectra at room temperature

Fig.2 shows the photoluminescence spectra from the near interface region of the grown layers. From Fig.1, the spectra marked #1, #2 and #3 correspond to the alloys of (x=0.6, y=0.8), (x=0.85, y=1) and (x=0.25, y=0.4), respectively. For the sample #2, which is GaAs-ZnSe pseudo-binary alloy, the band gap energy is 1.50 ± 0.05eV according to ref.[4]. However, for the samples of #1 and #3, the estimation is difficult in this stage. If we assume a linear relation of Eg on alloy component, their Eg values are calculated as 1.86eV and 2.02eV, respectively. These values were placed in the figure. It is clearly observed that the highest PL emission energy in each spectrum corresponds to the Eg value. Therefore we may roughly understand the band gap energy of quasi-ternary alloy.

4. Conclusion

Liquid phase epitaxial growth of Zn-Ga-As-Se quaternary alloy was investigated. When pure Ga saturated with GaAs and ZnSe was used as the growth solution, the grown layers were quasi-ternary alloy composed of GaAs, ZnSe and Ga_2Se_3, namely $(3GaAs)_x\{(3ZnSe)_y(Ga_2Se_3)_{1-y}\}_{1-x}$, where the alloy composition y was kept at 0.8 during the growth, while the composition x increased from 0.6 to 0.9 along the growth direction. When Zn was added to initial Ga, the alloy composition y increased to 1. As the result, pseudo-binary alloy of $(GaAs)_x(ZnSe)_{1-x}$ was obtained. On the contrary, supply of Se vapor pressure led the growth of alloy containing more Ga_2Se_3 component. These fundamental behaviours of this alloy system are useful in fabrication of photonic devices.

References

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