Influence of MBE Growth Temperature on the Sulfur Compositional Variation of ZnSSe Epitaxial Layers on GaAs Substrates

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In this work, we reported the sulfur compositional variation of ZnS_xSe_{1-x} epitaxial layers with growth temperature and BEP ratio of ZnS/Se(P_{ZnS}/P_{Se}) grown on GaAs substrates by molecular beam epitaxy. The sulfur composition of ZnSSe epitaxial layers was varied sensitively on the growth temperature and show different linear relationship with growth temperature and BEP ratio of ZnS/Se(P_{ZnS}/P_{Se}), which revealed -0.104 %/℃ at (P_{ZnS}/P_{Se})=0.30 and -0.052 %/℃ at (P_{ZnS}/P_{Se})=0.158 respectively. A reference data for the accurate control of the sulfur composition and the growth of high quality ZnSSe/GaAs epitaxial layers was provided.

Keywords : ZnS_xSe_{1-x}, Compositional Fluctuation, Lattice Mismatch, Beam Equivalent Pressure(BEP), Dual-chamber Molecular Beam Epitaxy.

1. INTRODUCTION

Since the first demonstration of lasing from II-VI semiconductor diode[1], many advances in the field of II-VI visible wavelength semiconductor laser diodes have been reported[2,3]. ZnS_xSe_{1-x} is a ternary compound semiconductor with a direct bandgap between 2.68 eV and 3.66 eV at 300 K. The usefulness of this material results from the possibility to tailor the bandgap and the lattice constant by adjusting the sulfur composition in the alloy. Therefore, this material can be used electrical and optical confinement in blue laser or modulator. GaAs is a widely used substrate material for the growth of II-VI compound semiconductors because of its availability in very good quality and the fairly low lattice mismatch to ZnSe and ZnSSe. In spite of slightly different lattice mismatch, there are problems of alloy fluctuation and defects in the ZnSSe epitaxial layers[4,5]. These problems have always been the most important issue for the realization of device life-time. For a long-lived laser diode, the defect density must be minimized[6]. In the case of control of Mg composition in ZnMgSSe, it is known that the sticking coefficient of Mg is relatively constant, but the S sticking coefficient can be varied over a wide range[4]. The compositional fluctuation is directly related to the defect density[7]. Therefore, minimizing alloy disorder of composition in ZnSSe and ZnMgSSe is important to reduce defect density. The sticking coefficient of S in ZnSSe and ZnMgSSe is very sensitive to growth temperature. The sensitive control of sticking coefficient of S is recommended for the growth of high quality alloy semiconductor[8]. Therefore, the growth parameters have to be optimized in order to reduce the alloy fluctuation during epitaxial growth. In the case of using ZnS source for the growth of ZnSSe and ZnMgSSe epitaxial layer, there are some problems such as restriction in sulfur compositions, effect of radiation during growth, etc. In most MBE growth for ZnSSe epitaxial layer, however, solid ZnS is used as the sulfur source because of safety of treatment and convenience of flux control[9]. In this work, we have grown ZnS_xSe_{1-x} epitaxial layers using ZnS as the sulfur source near lattice match condition($0 < x < 0.12$) on the GaAs(100) substrates and investigated growth temperature dependence of the samples by double-crystal X-ray(DCX) measurements.

2. EXPERIMENTAL PROCEDURE

The ZnS_xSe_{1-x}/GaAs structures were grown in a dual-chamber molecular beam epitaxy (MBE) system. One growth chamber is used exclusively for the growth of II-VIs materials, and the other chamber for the growth of III-Vs and preparation of GaAs substrates used for the epitaxial growth of ZnS_xSe_{1-x}. The GaAs epitaxial layers were grown at 560 ℃ under As-rich condition with a C(4×4) surface reconstruction. The thickness of the GaAs epitaxial layer was typically 0.5 μm. Subsequent to the GaAs epitaxial layer growth, the substrates were moved through the ultrahigh vacuum module to the II-VI chamber for growth. After moving to II-VI chamber, they were quickly heated up to 350 ℃ to prevent the interaction between the fresh GaAs surface with the background species in the II-VI growth chamber, and were exposed by Zn flux for 3 min. Then, the samples were cooled down to the 280 ℃ for the ZnSe buffer layer growth, of which layer were grown typically 100 Å before the growth of the ZnSSe epitaxial layers. Zn(6N), Se(6N) and ZnS(6N) were used as source materials. The beam equivalent pressure(BEP) of Zn, Se and ZnS was measured by ion gauge flux monitors, and flux was controlled by adjusting the cell temperature. We grew three series of ZnSSe epitaxial layers on the ZnSe/GaAs buffer layers on GaAs substrate. The one of three series samples were grown at 280 ℃ with various BEP ratio of ZnS/Se(P_{ZnS}/P_{Se}), and the another series were grown at two different BEP ratio of ZnS/Se(P_{ZnS}/P_{Se})=0.158 and 0.30 with various growth temperature between 260 ℃ and 325 ℃. All the growth temperatures were controlled with infrared optical pyrometer system. The thickness of all the ZnSSe epitaxial layers is approximately 0.4~0.6 μm, and its growth rate is ~0.5 μm/hr. The grown epitaxial layers were analyzed by double crystal X-ray diffraction(DCX) measurements for the (004) symmetric reflections.

3. RESULTS AND DISCUSSION

Fig. 1 shows the DCX rocking curves for ZnSSe epitaxial layers grown with various BEP of ZnS. The beam pressure were kept 5×10-7 Torr and 1.2×10-6 Torr for Zn and Se source, respectively and the growth temperature was kept at 280 ℃. The ZnSSe(004) peak shifts toward higher Bragg's angle with increasing BEP ratio of P_{ZnS}/P_{Se}. This result indicates that the sulfur composition in the ZnSSe epitaxial layers should depend on the flux ratio of ZnS and Se. The rocking curves show several narrow peaks around main ZnSSe(004) peak except grown with P_{ZnS}/P_{Se}=0.350. In the case of P_{ZnS}/P_{Se}=0.350, the epitaxial layer was relaxed by lattice mismatch to GaAs substrate. with increased sulfur composition.

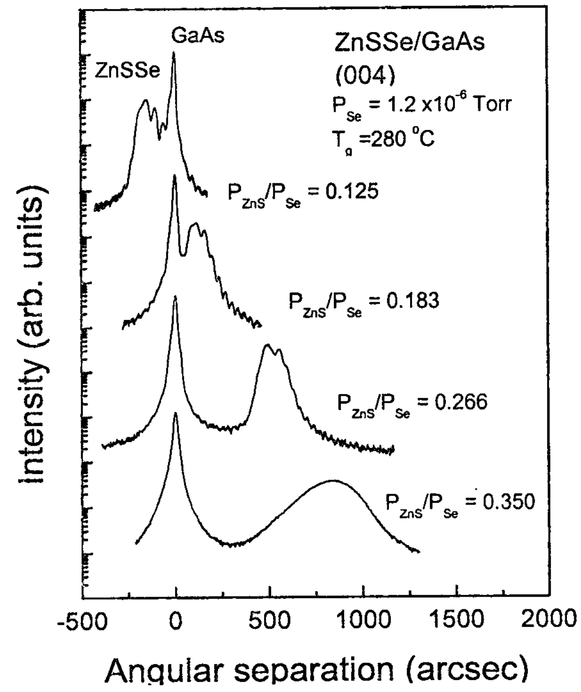

Fig. 1. DCX rocking curves for ZnSSe/GaAs grown with various BEP(P_{ZnS}/P_{Se}) ratio at 280 ℃.

The several narrow peaks around main ZnSSe(004) peak are generated by the interference of X-ray between surface and interface, and known as pendellosung fringes[10]. From the interference peaks, the epitaxial layers quality can be expected a high quality pseudomorphic heterostructure, clear surface and interface. However, the X-ray rocking curves of pseudomorphic ZnSSe(004) epitaxial layer show asymmetric shape and fringes distribution. This asymmetric distribution of interference peaks is caused by interference effects between regions with similar lattice constants, and the observations are consistent with a gradual change in the alloy composition as discussed in a previous report[4].

The dependence of sulfur composition with BEP ratio of P_{ZnS}/P_{Se} is shown in Fig. 2. This result shows that the sulfur composition of ZnSSe epitaxial layers depend on linearly up to $x=0.12$ as a function P_{ZnS}/P_{Se}. The sulfur composition, however, can be varied not only with ZnS flux but also with growth temperature.

The growth temperature dependence of sulfur composition is shown Fig. 3 and Fig. 4. Fig. 3 shows the DCX rocking curves as function of growth temperature between 260 ℃ and 310 ℃ with $P_{ZnS}/P_{Se}=0.158$. The ZnSSe(004) main peaks shift toward higher Bragg's angle with decreasing growth temperature. The shift of the ZnSSe(004) peaks is in agreement with the incorporation of sulfur in ZnSSe epitaxial layer with decreasing growth temperature. As decreasing growth temperature, the ZnSSe(004) peaks show broadening of

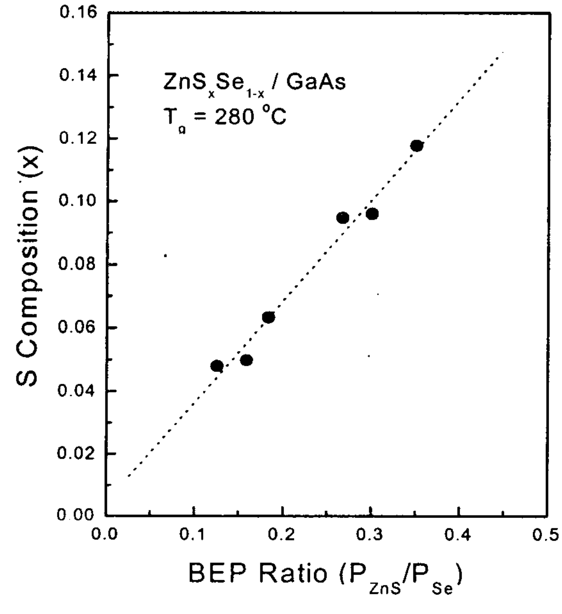

Fig. 2. The S compositin of ZnSSe epitaxial layers grown at 280 ℃ with various BEP(P_{ZnS}/P_{Se}) ratio.

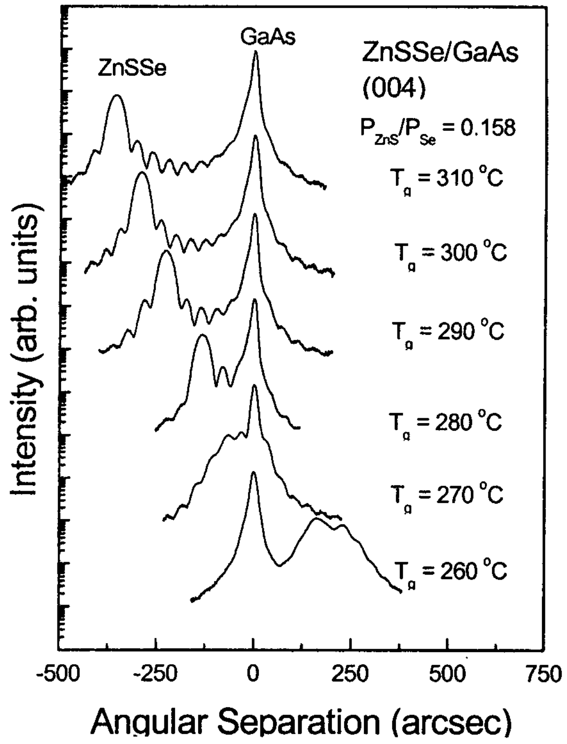

Fig. 3. DCX rocking curves for ZnSSe/GaAs grown with BEP(P_{ZnS}/P_{Se}=0.158) as function of growth temperature.

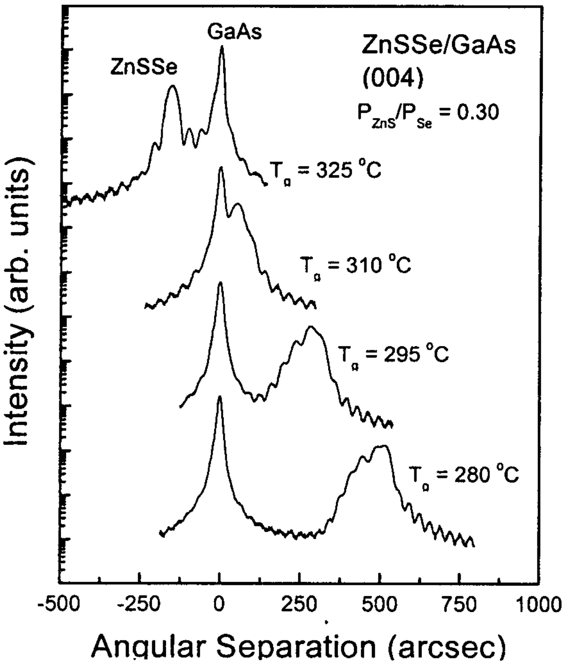

Fig. 4. DCX rocking curves for ZnSSe/GaAs grown with BEP(P_{ZnS}/P_{Se}=0.30) as function of growth temperature.

full width of half maximum (FWHM) and asymmetric shape. The FWHM of (004) reflection of ZnSSe epitaxial layers grown above 280 ℃ is 32 ~ 35 arcsec and also has interference peaks, which results indicate the high crystalline quality of the layers. In the lower growth temperature(< 280 ℃), however, the samples of ZnSSe(004) peaks also have interference peaks, but they are asymmetrically broadened(FWHM; 40 ~ 60 arcsec). For the comparison of ZnSSe epitaxial layer grown at different condition, the DCX rocking curves as function of growth temperature between 280 ℃ and 325 ℃ with $P_{ZnS}/P_{Se}=0.30$ are shown in Fig. 4. The rocking curves show similar behavior as shown in the results of Fig. 3.

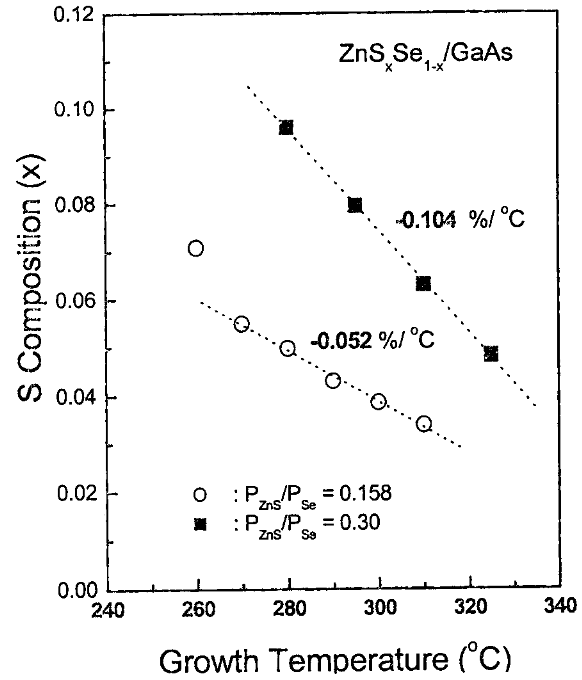

Fig. 5. The variation of S composition of ZnSSe epitaxial layers for the growth temperature.

Fig. 5 shows the dependence of sulfur compositions of ZnSSe epitaxial layer on growth temperatures with P_{ZnS}/P_{Se} = 0.158 and 0.30. Although the growth is under different condition of P_{ZnS}/P_{Se}, the results show good linearity of sulfur composition as a function of growth temperature, and also show different variation with P_{ZnS}/P_{Se}. The variation of sulfur composition with growth temperature shows higher variation at high P_{ZnS}/P_{Se} flux ratio and is found to be -0.104 %/℃, -0.052 %/℃ at P_{ZnS}/P_{Se}=0.30, 0.158, respectively(The sample grown at 260 ℃ is excepted in this linear fitting). The sulfur sticking coefficient strongly depend on growth temperature as shown in the results described above. Therefore, we believe that the asymmetrical broadening of the samples grown at lower temperatures is caused by the widely changed temperature during growth. Additionally, the significant asymmetrical broadening of x-ray rocking curves is measured from the samples grown below 270 ℃(P_{ZnS}/P_{Se}=0.158) and 295 ℃ (P_{ZnS}/P_{Se}=0.30), respectively. This results show the fluctuations of alloy composition during growth and also vary with P_{ZnS}/P_{Se} flux ratio. The above results can be analyzed that they could be affected by the thermal radiation of high temperature cell. The ZnS source cell keeps up normally to 800 ℃ for reasonable flux. Therefore, the surface temperature (below 300 ℃ in this study) could highly affect lower growth temperature and high flux ratio by thermal radiation. And also as another possible reason of the results, they could be affected by infrared pyrometer temperature control system through thermal radiation during growth. The growth temperature of substrates during growth is controlled with infrared pyrometer and thermocouple which measured the front of sample and the back side of substrate holder, respectively. In this study, the infrared optical pyrometer control method has been employed to implement the substrate temperature control during the epitaxial layer growth in order to avoid problems associated with inconsistent thermocouple contact to the substrate holder. However, the use of the optical pyrometer is complicated by the reflections of the infrared radiation at the epilayer interface or high temperature cell of molecular beam source(specially in this case; ZnS source cell)[4].

As shown above results, a prediction of the expected pyrometer reading is made for each epitaxial layer growth to control the substrate temperature at a constant value. Moreover, the informations of grown epitaxial layers with the variation of flux ratio and the growth temperature, shown in this study are important for the accurate prediction of surface temperature during growth. The above analysis can be used as reference data of the growth temperature optimization for the high quality MBE growth of ZnSSe and ZnMgSSe epitaxial layers.

4. CONCLUSIONS

In summary, we have investigated sulfur compositional variation with growth temperature of ZnS_xSe_{1-x} epitaxial layers grown on GaAs substrates by MBE using Zn, Se and ZnS sources. The BEP ratio of ZnS/Se(P_{ZnS}/P_{Se}) and the growth temperature dependence of S compositions were investigated. The S composition of ZnSSe epitaxial layers is varied sensitively on the growth temperature. The results show different linear relationship between the epitaxial layer sulfur composition and growth temperature with BEP ratio of ZnS/Se(P_{ZnS}/P_{Se}) which revealed -0.104 %/℃ at P_{ZnS}/P_{Se}=0.30 and -0.052 %/℃ at P_{ZnS}/P_{Se}=0.158, respectively. This results allow us to control the sulfur composition more accurately and also provide information for the control of the compositional fluctuation.

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