Characterization of GaAs/Zn(S, Se) Multi-Layered Structures Grown by OMVPE

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We report fabrication of multi-layered structures of GaAs/Zn(S,Se) lattice-matched system by OMVPE. Since optimum growth temperature for GaAs is above 600°C and for ZnSe below 500°C, for the growth of multi-layered structures we performed low temperature growth (470°C) of GaAs by photo-assisted OMVPE. This resulted in smooth growth of GaAs films with reduction in carbon contamination confirmed by PL and SIMS measurements and enhancement of Hall mobility. Hence we succeeded in fabrication of ZnSSe(300nm)/GaAs(100nm)/ZnSSe(300nm) double-hetero (DH) structure and superlattice (SL). PL of the DH structure subjected to thermal annealing showed no appreciable Zn diffusion in GaAs and thermal stability at interface upto 550° C.

1. INTRODUCTION

Special interest has grown, recently, on interfamily quasi-lattice matched structures of III-V and II-VI semiconductors^{1,2)}. In these systems, there exist large band discontinuity and large differences in refractive indices between the constituent layers, hence these structures can show new functionality for devices such as second harmonic generators, heterojunction bipolar transistors, heterojunction photo transistors, and solar cells. For this purpose, GaAs/Zn(S,Se) system is a suitable candidate but is least studied for multi-layered structures. The wider bandgap of Zn(S,Se)(>2.67eV at RT), compared to that of $Al_xGa_{1-x}As$ (2.0eV for x=0.5) also suggests a variety of device application where Zn(S,Se) may act as alternative to AlGaAs.

Much work have been reported on the epitaxial growth of Zn(S,Se) on GaAs, however little is known about the growth of GaAs on Zn(S,Se). This is because the optimum growth temperatures of GaAs and Zn(S,Se) are quite different in conventional growth techniques such as organometallic vapor-phase epitaxy

(OMVPE) and molecular beam epitaxy (MBE). In these systems, optimum growth temperature for GaAs is usually above 600°C, while for ZnSSe below 500°C. More recently, migration enhanced epitaxy (MEE) is applied for this purpose, but a complicated procedure in which As₄ predeposition at room temperature and subsequent thermal annealing is necessary prior to the GaAs growth²⁾.

In this paper, we investigated growth conditions for the GaAs/Zn(S,Se) multilayered system on GaAs substrates by OMVPE and characterized its properties for the first time, with special attention to the problem of interdiffusion at GaAs and Zn(S,Se) interface.

2. EPITAXIAL GROWTH

2.1 Growth System

For the practical fabrication of GaAs/ Zn(S,Se) multi-layered structures, we must grow good quality GaAs at a low temperature (< 500° C). For this purpose, we performed photo-assisted OMVPE growth by which alkyls in source precursors may be effectively eliminated at the growth surface^{3,4)}. The OMVPE growth was carried out by using a horizontal quartz reactor specially designed for photo-irradiation (Samco International Inc. model MCV-210) at low pressure (200Torr). A 500W xenon lamp with total irradiation power of 42mW/cm² was used as a light source.

2.2 Growth of GaAs (Photo-OMVPE)

For the growth of GaAs, we used triethylgallium (TEGa) and triethylarsenic (TEAs) as source precursors. The use of TEAs instead of AsH₃ is not only for the safety reason but also for its lower decomposition temperature. The growth temperature was around 500°C. The problem of high carbon contamination associated with TEAs and low temperature growth was mitigated by xenonlamp irradiation, where we confirmed reduction in carbon concentration by photoluminescence (PL) and SIMS analysis. Hall measurements showed enhancement in mobility due to the irradiation. These results clearly indicates improvement in quality of GaAs grown at low temperature as a result of light irradiation. Also smooth surface was observed by the irradiation. Details of this work appears elsewhere⁵⁾.

2.3 Growth of Zn(S,Se)

For the growth of ZnSe and ZnSSe, we used the source precursors diethylzinc (DEZn), dimethylselenium (DMSe), and diethylsulfur (DES). The sulfur composition was adjusted by the DES flow rate. We did not irradiated light during the growth of Zn(S,Se).

2.4 Growth of Multi-Layerd Structures

The uniform growth of GaAs on Zn(S,Se)was performed by the following techniques: (1)lattice-matching at the growth temperature, (2)sufficient preflow of TEAs with irradiation, and (3)Zn-stabilized surface of Zn(S,Se). In this manner, we succeeded in fabrication of GaAs/Zn(S,Se) multi-layered structures at 470°C.

3. CHARACTERIZATION

3.1 Structural Properties

First, we describe structural properties of a ZnSSe(300nm)/GaAs(100nm)/ZnSSe(300nm) double-hetero (DH) structure on a GaAs substrate. Cross sectional view of secondary electron microscope (SEM) photograph of this sample is shown in Fig.1. In-depth profiling of the constituent elements in Auger electron spectroscopy (AES) is shown in Fig.2, where yield of S-originated signal is not shown because it is very small and makes the figure more complicated. In this figure, the rapid decrease in Zn originated signal with sput-



Fig.1. Cross sectional SEM photograph of ZnSSe/GaAs/ZnSSe DH structure.



Fig.2. In-depth Auger profiling of constituent elements in ZnSSe/GaAs/ ZnSSe DH structure.

tering the first layer is probably due to charge-up rather than to concentration variation. These SEM and AES studies confirm the fabrication of GaAs/Zn(S,Se) DH structure.

We also attempted the growth of GaAs/ Zn(S,Se) superlattices (SLs). The X-ray diffraction obtained for a SL is shown in Fig,3. This pattern shows sharp peaks for $CuK\alpha_1$ and $CuK\alpha_2$ from GaAs substrate and three peaks from the SL (n=0 and two satellite peaks n=+1 and +2), from which the period of the SL was calculated as 40nm.

3.2 Annealing Effects

For the interfamily heterostructures, interdiffusion of constituent elements is a serious problem which may degrade the performance of the structure. In our GaAs/ Zn(S,Se) systems, considering the diffusion coefficient of the constituent elements, Zn diffusion into GaAs and Ga diffusion into Zn(S,Se) would be most possible. In order to investigate the interdiffusion problems, we annealed the ZnSSe/GaAs/ZnSSe DH structure upto $650^{\circ}C$, and did PL and X-ray measurements.

For PL experiment we used He-Cd laser with 325nm wavelength and 500mW/cm² power. If Zn diffuses into the GaAs layer, Zn-related peak should appear in the PL measurements. PL performed at 4.2K of the ZnSSe/GaAs/ZnSSe DH structure (unannealed), however, dominantshowed a peak at 1.492eV (831.1nm) which 1y is related to carbon impurity and not to Zn Additional peak also in GaAs (Fig.4). appeared at 1.431eV (866.5nm), which seems to originated from some defects in GaAs. ZnSSe did not show apparent band-edge luminescence while a single layer ZnSSe on GaAs showed strong bandedge luminescence at around 2.83eV (this value depends on the S composition). This behavior may be due to flow of generated carriers into GaAs well. ZnSSe however did show two peaks at about 1.8eV (690nm) and 2.0eV (620nm) which are understood as selfactivated centers in ZnSSe.



Fig.3. X-ray diffract pattern $(\theta - 2\theta \mod \theta)$ of $(GaAs/ZnSSe) \times 11$ SL.



Fig.4. PL spectra of ZnSSe/GaAs/ZnSSe DH structure. Variation due to thermal annealing is also shown. Here, T_a denotes annealing temperature.

Annealing experiment was done upto The variation of PL spectrum due to 650°C. the annealing, shown in Fig.4, resulted in (1) no appearence of Zn-related peak from GaAs, (2) disappearence of PL peak at 1.431eV (866.5nm), (3) reduction in carbon-related peak intensity above 550°C, and (4)merging and enhancement of two self activated centers SA1 and SA2 from ZnSSe above 550°C. These results are very useful as they indicate no significant interdiffusion of Zn upto 650°C investigated and thermal stability at interface upto 550°C. However above 550°C enhancement of SA peaks in ZnSSe and reduction in C-related peaks in GaAs are indicative of the possibility of (1)either the Ga diffusion



Fig.5. Double-crystal X-ray rocking curves of ZnSSe/GaAs/ZnSSe DH structure. Variation due to thermal annealing is also show. Here, T_a denotes annealing temperature.

in ZnSSe and hence formation of V_{Zn} -Ga_{Zn} related defects or creation of Zn vacancies in ZnSSe due to V_{Zn} migration or both at high temperatures and (2)reduction in carrier flow from ZnSSe to GaAs well as a result of enhancement of SA centers in ZnSSe. The fairly stable interface upto 550°C may be attributed to the lattice-matching⁶.

Double-crystal X-ray diffraction measurements performed on the ZnSSe/GaAs/ZnSSe DH structure shows two peaks besides the highest peak originating from the GaAs substrate (Fig.5). One of these two peaks should be from the ZnSSe layer but the other peak cannot be labeled at present, which reduces above 550°C. Annealing upto 580°C did not result in noticable variation in FWHM of the rocking curves, but annealing at 650°C shows increase in the FWHM value. This data are also in accordance with our PL data and confirms possibility of no significant degradation upto 550°C, i.e., thermal stability.

4. CONCLUSIONS

We could at low temperature grow good quality multi-layered structures of GaAs/ Zn(S,Se) by OMVPE (photo-OMVPE for GaAs epilayers) where interdiffusion specially Zn in GaAs upto 650°C temperature is suppressed due to an effect of lattice matching and thermal stability is achieved upto 550°C. Above 550°C, self-activated centers (V_{Zn} -Ga_{Zn}) in ZnSSe enhances possibly due to Ga diffusion or formation of Zn vacancies or both at high temperature.

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