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Thermal Stability and Interdiffusion at ZnSe/GaAs Interface

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We report effect of annealing at the interface of ZnSe/GaAs heterostructures grown on sulfur passivated GaAs by ALE and MOMBE. For this, we performed annealing in the temperature range of 300-500°C and studied by PL, SIMS and double crystal X-ray techniques. Results show that PL intensity of self-activated centers created due to interdiffusion at 500°C in conventionally grown sample is 14 times higher than in S-passivated sample. SIMS data show that Ga and As concentration in ZnSe epilayer is 2-4 times less in S-passivated materials. FWHM of X-ray rocking curves are much reduced as a result of sulfur passivation. These features suggest that heterostructures are thermally stable in sulfur passivated materials and sulfur passivation is an important tool for the fabrication of higher quality heterostructures of II-VI and III-V semiconductors.

1. INTRODUCTION

Heterostructure of II-VI and III-V semiconductors such as ZnSe and GaAs are of current interest for optoelectronic devices. This is because, ZnSe has bandgap twice that of GaAs and ZnSe possesses a lattice constant close to that of GaAs. In addition to this, ZnSe being a wider bandgap material can replace AlGaAs in many device applications.

In these heterostructures, interdiffusion between constituent layers seriously degrades various properties of the material because the diffused elements act as electricaly active centers, e.g., Zn or Se from ZnSe to GaAs. High temperature processes in device fabrication technology (400-600°C) accelerate the interdiffusion and degradation phenomena. Besides the interdiffusion problem, migration of defects at high temperatures[1] is also possible and can cause recombination with other native defects[2,3]. From these point of view, investigation of interdiffusion problem and thermal stability is basically important for discussing the potentials of dissimilar material heterostructures[4-8].

In the present work, we have investigated effects of annealing on ZnSe/GaAs hetero structure grown on S-passivated GaAs by PL, SIMS and X-ray measurements and discussed the results in terms of role of S-passivation and possible diffusion at the ZnSe/GaAs interface.

2. GROWTH

For the growth of ZnSe on GaAs, we used dimethylzinc (DMZn) and dimethylselenium (DMSe) as source materials for Zn and Se which were cracked at 950°C and 850°C, respectively, through tantalum crackers and were supplied simultaneously or alternatively to growth chamber. Here, for simplicity, we will refer the growth with simultaneous gas supply as MOMBE and that with alternative gas supply as atomic layer epitaxy (ALE) modes. The growth temperature for MOMBE mode was 300°C and for ALE mode 200°C.

We have used two different methods of GaAs surface pretreatment before the growth[9]. In the conventional manner, after degreasing and etching in H_2SO_4:H_2O_2:H_2O (5:1:1) solution, the substrate is dipped in water for the formation of a clear oxide layer and is then loaded into the chamber and heated at 600-750°C without As overpressure to remove the oxidized layer. Growth was initiated after cooling to the growth temperature. In the second case, i.e., S-passivation case, after degreasing and etching the GaAs substrate (as above), it was immediately dipped into $(NH_4)_2S_x$ solution for few minutes and then loaded into the chamber and preheated to about 290-420°C to desorb the excess sulfur. Growth started immediately after cooling to the growth temperature.

3. CHARACTERIZATION

Interdiffusion at the interface of hetero structutures is a serious problem and may result in the altered device characteristics. In ZnSe/GaAs heterostructures, considering the diffusion coefficient of the constituent elements, Zn diffusion into GaAs and Ga diffusion into ZnSe are most likely candidates. In order to investigate thermal and interdiffusion stability, we annealed ZnSe/GaAs structure upto 500°C and performed PL, SIMS and X-ray measurements.

PL measurement was carried out using He-Cd laser with 325nm wavelength and

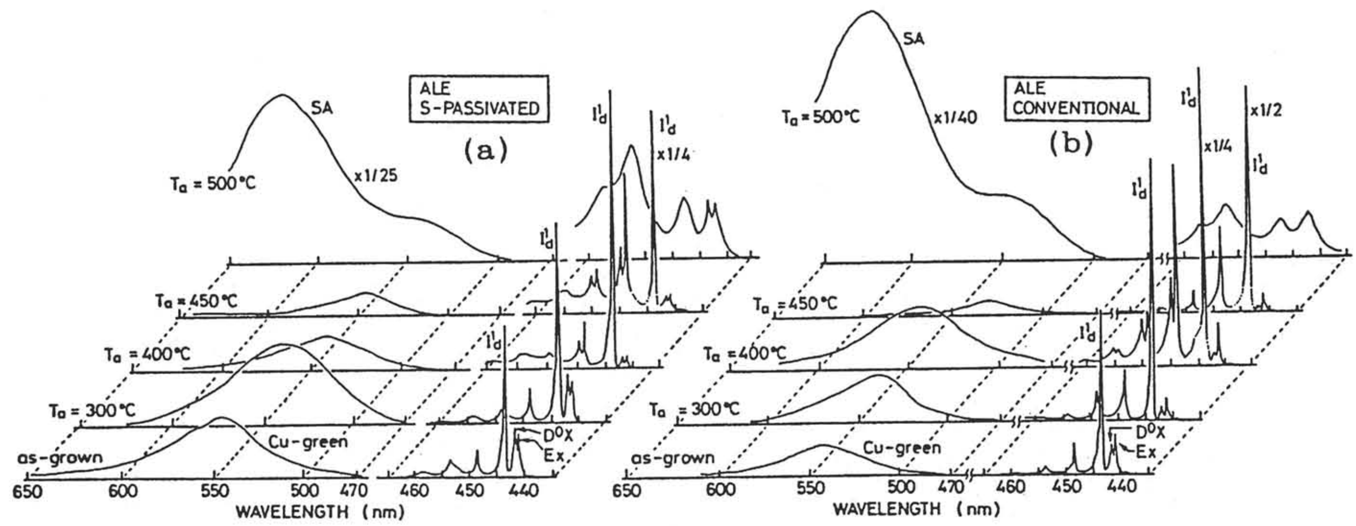

Fig.1 PL spectra of ALE grown ZnSe/GaAs heterostructure; (a)-$(NH_4)_2S_x$ pretreated, (b)-conventionally pretreated, GaAs surface. Variation in PL spectra as an effect of annealing temperature are shown. Here T_a denotes annealing temperature.

500mW/cm^2 power. PL spectra for 0.12μm thick pseudomorphic ZnSe grown by ALE onto $(NH_4)_2S_x$ pretreated and onto conventionally pretreated substrates are shown in Figs.1-a and 1-b respectively. PL spectra for all these samples exhibit well known band-edge luminescence from ZnSe designated as radiative recombination from Ex (free exciton), D^0,X (exciton bound to neutral donnor), A^0,X or I_1^d (exciton bound to neutral shallow acceptor or deep acceptor) and their phonon replicas LO_1, LO_2, and LO_3. Also appears is the peak related to Cu-green DAP (donor- acceptor pair - Cu^0,D^0).

Annealing experiment was performed upto 500°C. The effects of annealing on PL spectra are also shown in Figs.1-a,b and on the variation in the PL peak intensities (normalized with respect to Ex peak intensity) are plotted in Fig.2. These figures indicate in ALE grown (both with and without sulfur passivation) samples 1) creation of self activated centers (SA) at about 450-500°C, 2) increase in the Cu-green peak intensity with annealing temperature, 3) increase in I^1_d peak intensity with temperature upto 450°C then great reduction at 500°C. From this, it looks that as an effect of annealing Ga diffuses into ZnSe and possibly forms V_{Zn}-Ga_{Zn} complex structures resulting in creation of self-activated centers in ZnSe. At high temperature possibility of migration of V_{Zn} also exist which combines with diffused Ga and form V_{Zn}-Ga_{Zn} pairs. In addition to this, decrease in the intensity of I^1_d (related to deep acceptor V_{Zn} or Cu) with temperature also indicates the possibility of V_{Zn} migration and combination with diffused Ga_{Zn} at higher temperature. Increase in Cu-green (Cu,D^e - DAP) intensity may be due to migration of Cu (I^1_d related) at higher temperatures and recombination with D^e and

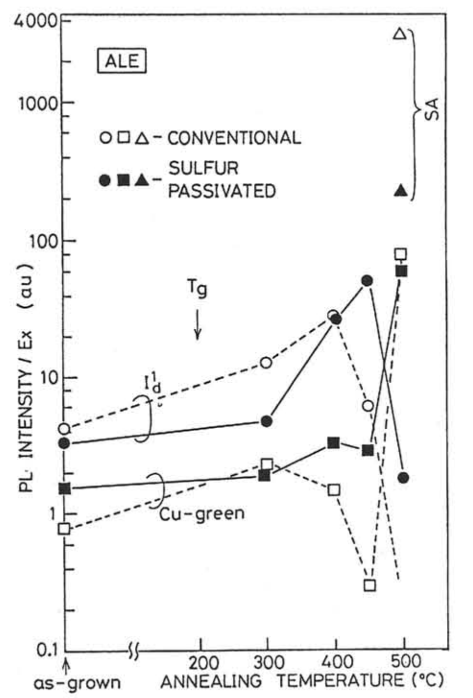

Fig.2 Variations in PL peak intensi- ties of I^1_d, Cu-green and SA centers in ALE grown ZnSe/GaAs heterostructure as a function of annealing temperature Here T_g denotes growth temperature.

hence formation of (Cu^0,D^0) DAP. Migration of V_{Zn} and formation of SA centers in electron irradiated bulk ZnSe at higher annealing temperatures has also been reported by electron paramagnetic resonance (EPR) investigations[1].

Next, if we pay attention to the intensity of SA emission in ALE grown samples we find that it is 14 times higher in the conventionally grown sample than in the

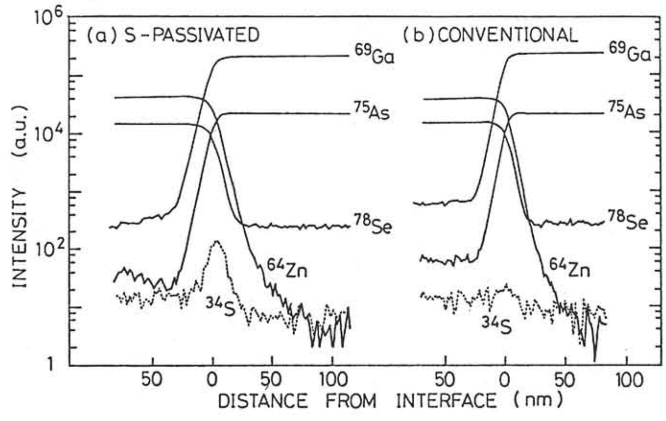

Fig.3 SIMS data for ALE grown ZnSe/GaAs heterostructure, annealed at 500°C

S-passivated sample. This suggests that the diffusion at the ZnSe/GaAs interface is highly controlled due to an effect of S-passivation of GaAs surface. This means that the surface of GaAs which has large density of surface states forms As-S and Ga-S bonds on the surface, in presence of sulfur. These bonds acts as barrier for the interdiffusion between GaAs and ZnSe, and restricts Ga diffusion into ZnSe in S-passivated samples.

We obtained similar results for MOMBE grown samples and that strongly supports to our above explaination, details of which appears elsewhere[10].

Secondry ion mass spectroscopy (SIMS) measurements (Fig. 3) performed on 500°C annealed sample of ALE (0.12mm) grown on with and without S-passivated GaAs shows that Sulfur remains at the interface of S-passivated ZnSe/GaAs heterostructure and that Ga and As concentration in ZnSe epilayer is 2-4 times less in S-passivated materials. These results strongly supports to PL data and confirms that S-passivation acts as barrier against interdiffusion.

Double crystal X-ray measurements performed on as-grown and annealed samples of ALE (0.12μm) and MOMBE (0.12μm and 1μm) showed presence of one peak related to ZnSe beside the highest peak originating from the GaAs substrate. FWHM determined from the rocking curve are tabulated in Table I, which show 1) FWHM of S-passivated, MOMBE both samples (0.12μm and 1μm) is much less as compared to that of conventionally grown samples indicating improved epilayer quality in S-passivated samples, 2) for ALE, since FWHM of conventionally grown sample itself is good, S-passivation did not show appreciable effect, and 3) annealing did not result in any systematic and appreciable variation in FWHM with temperature.

Table I FWHM (sec) of double-crystal X-ray rocking curve for ZnSe grown on conventionally pretreated GaAs (conv.) and on sulfur passivated GaAs (S-pass.).

annealing temp.(°C)	ALE grown d=0.12μm		MOMBE grown d=0.12μm		MOMBE grown d=1.0μm	
	conv.	S-pass.	conv.	S-pass.	conv.	S-pass.
as-grown	128	115	248	154	540	282
300	128	128	218	161	410	282
400	141	128	223	155	602	230
500	128	141	261	154	307	256

4. CONCLUSIONS

In conclusion, we have investigated thermally stability and interdiffusion at interfaces of MOMBE and ALE grown ZnSe/GaAs heterostructure grown on S-passivated GaAs, by performing annealing upto 500°C. We find that heterostructures are thermally stable in S-passivation materials. These features suggest that the sulfur passivation is an important tool for fabrication of high quality heterostructures of II-VI and III-V semiconductors. These heterostructures can result in fabrication of high performance devices like FET's, HBT's, and solar cells.

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