A Comparison of Zinc and Carbon Doped on the Atomic Interdiffusion of InGaAs/AlGaAs Quantum Wells Laser Structures After Annealing

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Abstract

We have compared a zinc and a carbon doped on the atomic interdiffusion of InGaAs/AlGaAs after annealing using Electrochemical capacitance voltage (EC-V), X-ray diffraction and photoluminescence (PL) measurements. Electrochemical capacitance voltage measurements revealed that the carrier concentration in the Zn-doped p^{++} GaAs contact layers decreased after annealing at 900°C for 60 sec, indicating that some of the Zn acceptors were passivated or outdiffused from the surface. In contrast to the C-doped samples, an increase of carrier concentration was observed after annealing. X-ray rocking curve confirmed this result where the amount of lattice contraction increase after annealing which is attributed to the presence of the substitutional carbon C_{As} . Photoluminescence results showed that a large energy shift was observed in the Zn-doped samples compare with C-doped samples. Photoluminescence measurements after etching to various depth showed similar luminescence defects in both Zn- and C-doped samples. Photocurrent measurements showed the quality of quantum well was improve after annealing in C-doped samples due to activation of carbon doped.

Keywords: Atomic intermixing, Carbon doped, InGaAs/AlGaAs QWs

1. Introduction

Thermal annealing is an essential in semiconductor device processing technique and is particularly useful for intermixing where high temperature annealing is required to initiate the intermixing between the barrier and quantum well regions. On the other hand, the high temperature annealing required for intermixing could adversely affect the quality of quantum wells and thus the device performance. Despite of this disadvantage, quantum well intermixing (QWI) has been widely used to modify the bandgap energy through the intermixing of constituent atoms between the barrier and quantum well regions. In addition to this, QWI can be used to tailor the new devices and has found applications in semiconductor lasers, waveguides, and optoelectronic integrated circuits¹⁾. There are several methods commonly used to initiate the well-barrier intermixing such as impurity induced disordering²⁾, impurity-free vacancy disordering³⁾, and ion implantation induced disordering⁴⁾. All these methods rely on the diffusion of defects across the heterointerfaces to initiate the interdiffusion process. Many studies have reported the effect of dopants on the intermixing process^{2,5,6)}, but the effect of dopant diffusion in actual optoelectronic devices has not received much attention.

In this report, we compare the atomic interdiffusion of InGaAs/AlGaAs/GaAs laser structures doped with zinc and carbon atoms after annealing. Thin p -clad InGaAs/AlGaAs QW laser structures were used for interdiffusion study. This particular structure uses an asymmetric design such that most of the optical field distribution lies in n -type

layers, near the substrate and only small part of the distribution is found near the top surface. The lasing parameters of this type of structure are comparable with those of standard well-behaved symmetric structures. In addition, this structure is well suited for intermixing in GaAs based system, where the diffusion length of Ga vacancies is of the order of 0.1 μm . For interdiffusion study, the InGaAs/AlGaAs laser structures were annealed at various temperatures in the range of 875-925°C to initiate the interdiffusion between the quantum well and barrier region as well as to measure the ability of the samples to retain their physical properties after thermal processing. Generally, photoluminescence measurements such as the PL intensity and PL line width were used to observe the change of samples properties after interdiffusion. The laser structures used in this study were doped with zinc and carbon atoms. Carbon is known to have less diffusivity in GaAs-based materials in comparison to the zinc⁷⁻⁹⁾. The degree of interdiffusion in both samples was also investigated.

2. Experiment

The laser structures used in this work were grown on n^{++} GaAs substrates using low pressure metal-organic chemical vapor deposition (LP-MOCVD). The details of these asymmetric InGaAs/AlGaAs laser structures have previously been reported¹⁰⁾. Two different structures were grown that differed only by the type of dopant used for p -type contact and cladding layers, in one case they were doped with Zn and in other C. Details of the structures are summarized in Table 1. After growth, the two samples were annealed under Ar flow in a rapid thermal

annealer at temperatures in the range of 875-925°C for 60 sec. During annealing the sample surfaces were protected using the GaAs proximity capping method to minimize arsenic loss. Photoluminescence (PL) measurements were performed at 77K to monitor the extent of quantum well intermixing. The PL set-up consisted of a frequency-doubled diode-pumped solid-state laser (at 532 nm) for excitation and an InGaAs

photodetector at the output slit of a 0.5 m monochromator. Doping profiles were measured using a Bio-Rad electrochemical voltage (EC-V) profiler model PN-4300PC. Finally, the sample strain was measured by Double-crystal X-ray diffraction (DCXRD) using a Bede QC2a system.

Table 1. Details of the layers of the asymmetric InGaAs/AlGaAs laser structures used in this work

Layer Type	Al composition index	Thickness	Doping
$p^{++}\text{GaAs}$	0.00	0.10 μm	$C > 1 \times 10^{19} \text{ cm}^{-3}$
$p \text{ Al}_x\text{Ga}_{1-x}\text{As}$	0.60	0.30 μm	$C \sim 1 \times 10^{18} \text{ cm}^{-3}$
Grading $\text{Al}_x\text{Ga}_{1-x}\text{As}$	0.60 $\rightarrow$ 0.20	0.16 μm	undoped
GaAs	0.00	1.8 nm	undoped
$\text{In}_{0.20}\text{Ga}_{0.80}\text{As}$		6 nm	undoped
GaAs	0.00	1.8 nm	undoped
$\text{Al}_x\text{Ga}_{1-x}\text{As}$	0.20	6 nm	undoped
GaAs	0.00	1.8 nm	undoped
$\text{In}_{0.20}\text{Ga}_{0.80}\text{As}$		6 nm	undoped
GaAs	0.00	1.8 nm	undoped
Grading $\text{Al}_x\text{Ga}_{1-x}\text{As}$	0.20 $\rightarrow$ 0.60	0.16 μm	undoped
$\text{Al}_x\text{Ga}_{1-x}\text{As}$	0.60	0.10 μm	$\text{Si}: 10^{17} \text{ cm}^{-3}$
Grading $\text{Al}_x\text{Ga}_{1-x}\text{As}$	0.60 $\rightarrow$ 0.30	0.02 μm	$\text{Si}: 10^{17} \text{ cm}^{-3}$
$\text{Al}_x\text{Ga}_{1-x}\text{As}$	0.30	0.22 μm	$\text{Si}: 10^{17} \text{ cm}^{-3}$
Grading $\text{Al}_x\text{Ga}_{1-x}\text{As}$	0.30 $\rightarrow$ 0.45	0.01 μm	$\text{Si}: 10^{17} \text{ cm}^{-3}$
$\text{Al}_x\text{Ga}_{1-x}\text{As}$	0.45	0.07 μm	$\text{Si}: 5 \times 10^{17} \text{ cm}^{-3}$
$\text{Al}_x\text{Ga}_{1-x}\text{As}$	0.45	2.00 μm	$\text{Si}: 10^{18} \text{ cm}^{-3}$
n^+ substrate			

3. Results and Discussion

3.1 Electrochemical profiling

Figure 1(a) and (b) show the carrier concentration as a function of depth for zinc and carbon doped samples, before and after annealing at 900°C for 60 sec. The first 0.1 μm corresponds to the highly doped $p^{++}\text{GaAs}$ contact layer, and the next 0.45 μm to the $p \text{ AlGaAs}$ cladding layer. Annealing significantly reduced the carrier concentration of the Zn-doped $p^{++}\text{GaAs}$ layers. There was also a relatively small reduction in Zn concentration of the AlGaAs cladding layers after annealing. This reduction could be due to Zn acceptor compensation or through the loss of Zn from the surface¹¹⁾. Very different results were observed for the samples doped with carbon. Annealing at 900°C increased the electrically active carrier concentration in the top

$p^{++}\text{GaAs}$ layers and the AlGaAs cladding layers by about 29% and by 58%, respectively. The increase of carrier concentration in the carbon doped sample is due to the removal of the C-C interstitial pairs that have been reported previously¹²⁾.

It is clearly seen from the EC-V results that very different behavior for zinc and carbon doped after annealing, suggesting that the diffusion mechanism involving is different. In the case of Zn-doped samples, most studies of Zn diffusion in Zn doped III-V quantum well structures reported that Zn diffusion operates via the interstitial-substitutional mechanism. Zn atoms diffuse into the quantum well region as charge interstitial Zn_i^+ and then move onto the group III atom sublattice to form immobile substitutional acceptor¹³⁾. There are two model that have been suggested for this. In the first model, the interstitial combines with a gallium vacancy to form the substitutional acceptor¹⁴⁾. According this model,

the Ga concentration will reduce since Zn interdiffusion take up vacant Ga sites. The second model is the "Kick-Out" model. In this model, Zn interstitial become substitutional acceptors by making the Ga atoms interstitial¹⁵. In our results, most likely that annealing the samples without an overpressure of Zn and As might cause Zn and As atoms outdiffusion from the sample surface. The outdiffusion of zinc and arsenic lead to in a reduction of zinc concentration in p^{++} contact layers. In the case of the C-doped samples, it is well known that carbon incorporates primarily as a substitutional acceptor on the As sublattice¹⁶⁻¹⁸. Annealing the samples with proximity capping leads to outdiffusion of As ions. As a result, additional arsenic vacancies are created which is allowing an increase incorporation of carbon to the arsenic, and this explain the increased of carrier concentration in C-doped samples.

Figure 1. EC-V profile of carrier concentration of Zn- and C-doped InGaAs/AlGaAs laser structures before and after annealing at 900°C for 60 sec.

3.2 X-ray diffraction

The DCXRD rocking curves for Zn- and C-doped samples before and after annealing at 900°C for 60 sec are shown in Figure 2. The features appearing on the left hand side of the main (GaAs) peak are related to the AlGaAs layers. The curves for both as-grown samples look similar except for an additional small peak to the right of the main peak in the C-doped sample. This peak is related to the slight tensile strain caused by the incorporation of the smaller C atoms in the highly doped p^{++} GaAs contact layer. It has been shown that if the carbon concentration is higher than about 10^{19} cm^{-3} , it causes lattice contraction since carbon has a smaller covalent radius

(0.77 Å) compared to As (1.20 Å) or Ga (1.26 Å)¹⁹. After annealing this peak becomes more pronounced (C-doped sample). This increase of lattice contraction by about 26% compared to the as-grown wafer is comparable to 29% electrical activation obtained from the EC-V measurement. In the case of Zn-doped samples, annealing at 900°C for 60 sec resulted in the smearing of the AlGaAs-related peaks. As shown in the next section, this is consistent with more pronounced intermixing caused by the interdiffusion of Zn across the QW/active region.

Figure 2. DCXRD spectra of Zn- and C-doped samples InGaAs/AlGaAs laser structures for as-grown and annealed samples.

3.3 Photoluminescence

Figure 3 shows the PL spectra of the Zn- and C-doped samples before and after annealing for 60 sec at various temperature ranging from 875°C to 925°C. The emission peak at 903 nm originates from the quantum well region. For the Zn-doped sample (Figure 3a), the peak from the quantum well consistently shifted to shorter wavelength with increasing annealing temperature. Larger wavelength shift was observed after annealing at 925°C and was followed by a significant reduction in the PL intensity. In addition to this the PL linewidths progressively broadened with annealing temperature. The larger wavelength shift for the Zn-doped samples is consistent with the higher Zn diffusivity in GaAs/AlGaAs. A smaller shoulder at 896 nm and a relatively broad peak at 942 nm were also observed after annealing at 925°C. These peaks are attributed to radiative transitions from point defects which were thermally generated during annealing as discussed later.

In the case of C-doped samples (see Figure 3b), only a slight blueshift was observed after annealing at 875°C and 900°C, while the PL intensities and PL linewidths are comparable to the as-grown samples. This indicates that only very little interdiffusion had occurred at these temperatures and the quality of the structures was preserved. At 925°C, the PL intensity decreased and was accompanied by a relatively large wavelength shift and slight broadening of the

linewidth. In comparison to the Zn-doped samples, we observed a much smaller atomic interdiffusion in the C-doped samples. This is due to group-III sublattice (Al,Ga) is the dominant mechanism involved, and the substitutional carbon on group-V sublattice may have little influence on the intermixing mechanism during annealing. In addition to this the substitutional C_{As} concentration in the C-doped samples is much lower than zinc interstitial (Zn_i^{+} in the Zn-doped samples). Similar to the Zn-doped samples, two smaller peaks at 896 and 942 nm were also observed in the C-doped samples annealed at 925°C. In both the Zn- and C-doped samples the broad peak at 896 nm (1.384 eV) disappears after removal of the top p^{++} GaAs contact layer. This peak may be related to a $Zn_{Ga}-V_{As}$ transition (1.37 eV)²⁰ or to a $V_{As}-C_{As}$ transition (1.41 eV)²¹ in the top p^{++} GaAs layer.

Figure 3. Low temperature photoluminescence spectra of Zn- and C-doped InGaAs/AlGaAs laser structures before and after annealing varying the temperature from 875°C to 925°C.

In order to investigate the additional peaks that appear in the PL spectra, the samples were etched to either a depth of 0.2 μm or 0.70 μm , corresponding to the removal of the top p^{++} GaAs layer and the QWs, respectively and then annealed. Figure 4 shows the 77K PL spectra of the etched samples taken before and after annealing at 925°C. Only the QW peak at 906 nm was observed in both the as-grown Zn and C-doped etched to a depth of 0.2 μm . In the as grown Zn- and C-doped samples etched to 0.7 μm depth, two peaks at 943 nm (1.315 eV) and 1060 nm (1.170 eV) were observed. It should be noted at this depth, we were probing the n-AlGaAs layers. Clearly these two

peaks were already present in the as-grown n-AlGaAs but were masked by the QW luminescence.

After annealing, the samples etched to a depth of 0.2 μm annealed showed a blue shift of the QW emission and two additional peaks at 943 nm and 1254 nm were observed. However, in the Zn-doped sample, the 943 nm peak was much stronger than that in the C-doped samples. Also after etching to depth of 0.7 μm and annealing the intensity of the 943 nm peak is diminished. This suggests that it was related to a defect peak that was enhanced during the annealing step and its concentration was influenced by the type of dopant present in the sample. Furthermore, it was also observed in the n-AlGaAs layers (samples etched to 0.7 μm) before and after annealing. Hence, we attribute this peak to a point defect complex related to the group-III species. In GaAs, two emission are reported at 77K, 1.32 eV related to Ga^{2-}_{As} and at 1.284 eV related to Ga^{2-}_{As} ²². Therefore it is possible that the peak observed at 943 nm is related to these antisites. However, there are few studies related to defect complexes in the case of moderate to high Al content AlGaAs.

Figure 4. Low temperature photoluminescence spectra of Zn- and C-doped InGaAs/AlGaAs laser structures after etching surface of the samples to different depths

The peak at 1254 nm was also observed in moderately Si-doped GaAs samples ($5 \times 10^{16} \text{ cm}^{-3}$)²³. Several other studies have reported the presence of this peak at 77K in Si-doped GaAs and correlated it with $Si_{Ga}-Si_{As}$ complex^{24,25}. On the other hand, Liang *et al.*,²⁶ interpreted this as the recombination luminescence of the donor-acceptor pairs $V_{As}-V_{Ga}$. In

our case, this peak becomes only prominent after annealing. Furthermore, its intensity was stronger in the Zn-doped compared to the C-doped sample. Although a lower intensity was observed in the samples etched to 0.7 μm depth (i.e. in the $n\text{-AlGaAs}$ layers), it is unlikely that this peak is related to the $\text{Si}_{\text{Ga}}\text{-Si}_{\text{As}}$ complex in our case since its intensity was stronger when the top $p\text{-AlGaAs}$ layers were present.

For both Zn- and C-doped samples etched to 0.7 μm after annealing, the 1060 nm peak diminishes in intensity and was accompanied by the appearance of the 1254 nm peak. This may be due to Si-related defect in $n\text{-AlGaAs}$ since it was not observed in the 0.2 μm etched samples. The intensity of the 943 nm peak remains essentially the same before and after annealing. The relatively stronger stability of this peak suggests that it might be due to more thermally stable defect, such as an antisite (Ga_{As}) as discussed earlier. In the case of Zn-doped samples, the defect/impurity related peaks are more prominent after annealing. Subsequently the quality of the QW luminescence is much inferior to that of the C-doped sample after intermixing. A summary of the observed defects peak for as-grown and annealed samples in both Zn- and C-doped etched samples as shown in Table 2.

Table 2. The observed defects peak for as-grown and annealed samples in both Zn- and C-doped InGaAs/AlGaAs etched samples.

Etched depth	As-grown	Annealed
0.2 μm (Zn)	No peaks	943 nm and 1254 nm
0.7 μm (Zn)	943 nm and 1060 nm	943 nm and 1254 nm
0.2 μm (C)	No peaks	943 nm and 1254 nm
0.7 μm (C)	943 nm and 1060 nm	943 nm and 1254 nm

4. Conclusion

A comparison of zinc and carbon doped on the atomic interdiffusion of InGaAs/AlGaAs/GaAs laser structures has been studied. The EC-V measurements show that some of the zinc acceptors are passivated or out-diffused from the surface after annealing while in contrast, part of the carbon dopant is activated. PL results from etched samples suggest the presence of higher concentration of point defects after annealing in the zinc doped sample than in the carbon doped samples. These point defects are responsible for degradation and larger blueshift of the QW emission in zinc doped sample in comparison to the carbon doped structures.

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