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Improved thermal stability of AlGaAs/GaAs/AlGaAs single quantum well by growth on Zn-doped GaAs (001)

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Abstract

The effects of Zn doping in the substrate on the thermal stability of GaAs/$Al_{0.24}Ga_{0.76}As$ single quantum well are investigated by 900 °C rapid thermal annealing and low-temperature (12 K) photoluminescence measurements. An improvement in thermal stability is demonstrated for structures grown on Zn-doped GaAs in comparison with those grown on semi-insulating and Si-doped GaAs substrates. It is likely that the Zn out-diffusion from the substrate to the quantum well region has lowered the Al–Ga interdiffusion coefficient.

Keywords: Diffusion; Gallium arsenide; Thermal stability; Zinc

1. Introduction

Quantum well (QW) structures are widely used in optoelectronic devices and other high speed and high power semiconductor devices. The thermal stability of quantum well structures are important for device processing and device reliability, it is a measure of the ability of a sample to retain its physical properties after thermal processing and is indicated in this work by photoluminescence (PL) peak energy and, to a lesser extent, by PL line width after annealing. Quantum well intermixing (QWI) between the well and barrier layers affects the thermal stability and has been the subject of numerous research works. QWI can be a nuisance as it degrades the crystal quality of the wafer and shifts the sub-band levels, thus limits the process temperature latitude. On the other hand, it can be a tool for the tailoring of new devices and has found applications in semiconductor lasers, transparent waveguides, and optoelectronic integrated circuits [1]. For example, QWI is often employed to fabricate non-absorbing mirrors in high power laser diodes. Intermixing between QW and adjacent barriers results in a change of the QW shape, which in turn, modifies the sub-band energies in the conduction band and the valence band [2]. As refractive index is directly related to absorption coefficient [3], intermixing also modifies the refractive index and can thus be applied to optoelectronic devices. Quantum well intermixing may be achieved thermally, both in the absence [4,5] and presence [6,7] of extrinsic impurities, as well as via pulsed laser irradiation [8].

Many studies have shown that Zn enhances the intermixing of GaAs/AlGaAs QW structure [5,9–13]. Thermal stability of GaAs/AlGaAs QW structures was studied at the early days of QWI [14–16]. In these studies, Zn was usually provided through Zn in-diffusion from external sources or by ion implantation or Zn out-diffusion from grown-in layers. Zn diffusion increases defect concentration in the QW regions (Column III vacancies and interstitials) [5]. Since interdifussion between Al and Ga atoms in the QW region increases with increasing defect concentration (usually Group III vacancies) [5], the thermal stability of GaAs/AlGaAs QW is reduced by Zn diffusion. Laser diodes with a partially intermixed QW active layer were fabricated by Zn out-diffusion from a Zn-doped p-cladding layer to the QW region [11]. The p-cladding layer was 1.5 μm

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thick and 60 nm from the quantum well. The sample was annealed at 660 °C for 37 min. It was found that the higher the Zn doping in the cladding layer, the higher the blue shift in the photoluminescence spectra. While high Zn concentration increases the Al–Ga interdiffusion, low Zn concentration can be used to reduce the Al–Ga interdiffusion in the quantum well region. Krames et al. [13] obtained improved thermal stability in GaAs/AlGaAs QW structures at high temperatures (850 °C) by using a 'blocking' Zn diffusion method at low temperatures (450–600 °C). The blocking Zn diffusion was performed by placing the sample and $ZnAs_2$ (Zn source) in a sealed ampoule and annealed together. The improved thermal stability was attributed to a Zn-diffusion induced reduction in the number of column-III vacancies in the active layers. In GaAs/AlGaAs system, a high concentration ($>10^{18}$ cm^{-3}) of Zn interstitial defects usually generates high concentrations of Group III vacancies and interstitials at high annealing temperatures (e.g. 850 °C), which will enhance the intermixing via enhanced Ga and Al interdiffusion [5,6]. However, in the case of Krames et al. [13], the annealing temperature was relatively low (450–600 °C), thus Zn atoms do not generate high concentrations of Group III vacancy and interstitial defects. Instead, Zn atoms occupy existing Group III vacancies, reducing Group III vacancies that would otherwise be available for Ga and Al interdiffusion at high temperature annealing (850 °C), thus the Zn impurity atom diffusion at low temperature actually improved the thermal stability of the GaAs/AlGaAs quantum well samples at high temperature. Many compound semiconductor devices are grown on doped GaAs substrates; the out-diffusion of the substrate dopants into the epitaxial layers may affect the physical properties of the device. To the best of our knowledge, however, there has been no report on the effects of doping in the substrate on QWI. For GaAs/AlGaAs quantum well structures grown on Zn-doped GaAs substrate, Zn out-diffusion will affect the Group III vacancy concentration in the active region, and thus affect the QWI at high annealing temperatures. In addition, the extra diffusion step at low temperatures (450–600 °C) as used by Krames et al. can be dropped as the blocking Zn diffusion can be achieved automatically during the sample growth.

In this work, we compare the effects of various GaAs substrate doping on the intermixing of undoped GaAs/$Al_{0.24}Ga_{0.76}As$ single QW structures. The samples grown on Si-doped and semi-insulating GaAs substrates show a significant blue shift in comparison to as-grown (i.e. un-annealed) respective samples, in agreement with earlier studies by, e.g. Cusumano et al. (Si-doped GaAs substrate) [17] and Ooi et al. (semi-insulating GaAs substrate) [18]. The sample with Zn-doped GaAs substrate, however, shows evidence of suppressed intermixing by Zn diffusion from the substrate into the QW structure. The enhanced thermal stability of the GaAs/$Al_{0.24}Ga_{0.76}As$ QW structure is attributed to a Zn-diffusion induced reduction in the number of column-III vacancies in the QW structure. The enhanced thermal stability and reduction in the number of column-III vacancies could be useful for device processing and improve the performance and reliability of devices like laser diodes, high electronic mobility transistors (HEMTs) and heterostructure bipolar transistors (HBTs).

2. Experimental procedures

Three samples were mounted on the same block by indium bonding and grown together in the same run by molecular beam epitaxy (MBE) on three commercially-available (001) GaAs substrates: semi-insulating substrate (SI-sample), Zn doped at $\sim 1\times10^{18}$ cm^{-3} (P-sample), and Si doped at $\sim 2\times10^{18}$ cm^{-3} (N-sample). The structures consisted of a 200 nm GaAs buffer layer, followed by a single QW structure consisting of a 4 nm GaAs layer sandwiched between two 50 nm $Al_{0.24}Ga_{0.76}As$ layers. The entire structure was capped with a 100 nm GaAs layer. All the epilayers were nominally undoped with a background p-type doping of approximately $(4\pm1)\times10^{14}$ cm^{-3}. The growth temperature was 580 ± 3 °C, as determined by a thermocouple on the backside of the sample plate, and the V/III beam equivalent pressure ration was approximately 10.

After growth, the samples were cleaved into 3 mm×3 mm pieces, and then rapid thermal annealed (RTA) in a rapid thermal processor (RTP) in flowing N_2 ambient. During the RTA process, the samples were placed between two semi-insulating GaAs substrates to prevent As loss. For all the annealing processes, the temperature ramp-up rate was fixed at 50 °C/s. To minimize run-to-run variations in the RTP system, all three types of samples (n-type, p-type, and semi-insulating substrates) were annealed together in the same run. After the annealing, the RTP chamber was quickly cooled down by flowing water in tubes wound around the annealing chamber. After annealing, low temperature (12 K) photoluminescence measurements were performed with an Ar ion laser beam (488 nm), a spectrometer, and a thermoelectrically cooled Si detector.

3. Results and discussion

Fig. 1 shows PL spectra collected from both the as-grown and 876 °C annealed samples. It is evident that the three as-grown samples showed an emission at 761 nm, indicating similar initial structures. All the annealed samples showed PL spectra blue-shifted by up to 56 meV, in comparison with the as-grown samples, presumably due to Ga–Al interdiffusion occurring at high temperatures. The PL collected from the sample grown

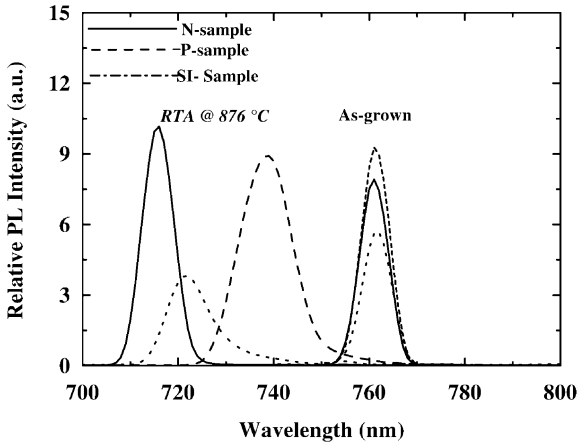

Fig. 1. 12 K PL spectra from as-grown samples and samples annealed together at 876 °C for 150 s. The samples are: N-sample, P-sample, and SI-sample.

on p-type substrate has the smallest blue-shift, suggesting that it is the most thermally stable. The PL peak energy varied by approximately 10 meV from run to run, likely due to poor temperature control of the RTP system (approx. ±5 °C from run to run). In the RTP system, a bank of lamps provides heating over an area suitable for a 6-inch diameter wafer. The maximum temperature difference between any two points on a 6-inch wafer is ±5 °C. Since the samples were placed close to each other (with a distance of approx. 2–3 mm between adjacent pieces) and at the center of a Si support wafer, the lateral temperature variation from sample to sample in the same run was insignificant.

In this work, the PL peak energy shift (difference) after annealing as compared to the data of as-grown sample is used as a measure of the thermal stability of GaAs/AlGaAs quantum well. The thermal stability here, refers to the resistance to changes caused by the thermal processing. The less shift after annealing, the higher the thermal stability. Shown in Fig. 2a is the blue shift of the annealed samples as a function of annealing time at a fixed annealing temperature of 876 °C. It can be seen that the P-sample is much more thermally stable than the SI-sample and the N-sample. For the 30 s annealing at 876 °C, the P-sample had a blue shift of 19.5 meV, compared to 46.3 meV for the SI-sample and 55.4 meV for the N-sample. The thermal stability under this annealing condition shows a noticeable increase. For the SI-sample, the general trend of increasing blue shift with annealing time is due to the increased diffusion length of Group III atoms with annealing time. The N-sample shows the largest blue shift, which is in agreement with other Yuan et al. [5]. This could be due to the out diffusion of Si from the substrate into the QW structure that enhances the Column III diffusion, and it manifests itself as enhanced blue shift in Fig. 2a.

Fig. 2b shows the blue shift of the annealed samples as a function of RTP temperature for a fixed annealing time of 30 s. Again, it is demonstrated that the Zn doping in the substrate improves the thermal stability of the GaAs/$Al_{0.24}Ga_{0.76}As$ QW structure grown on the substrate. The samples were more stable below 900 °C. This is in agreement with our earlier work that showed GaAs/AlGaAs QW structures grown by metalorganic chemical vapor deposition (MOCVD) at approximately 730 °C were thermal stable up to 900–920 °C [19]. In the work of Yuan et al. [19], the MOCVD-grown samples were annealed between 875 and 950 °C for RTA durations from 10 to 105 s, but the GaAs/AlGaAs quantum well sample showed little PL energy shift below 920 °C {Dash-dotted curve (unanodized sample) in Fig. 5 of Yuan et al. [19]}. For the MBE-grown sample shown in Fig. 2b, the wavelength shift of P-

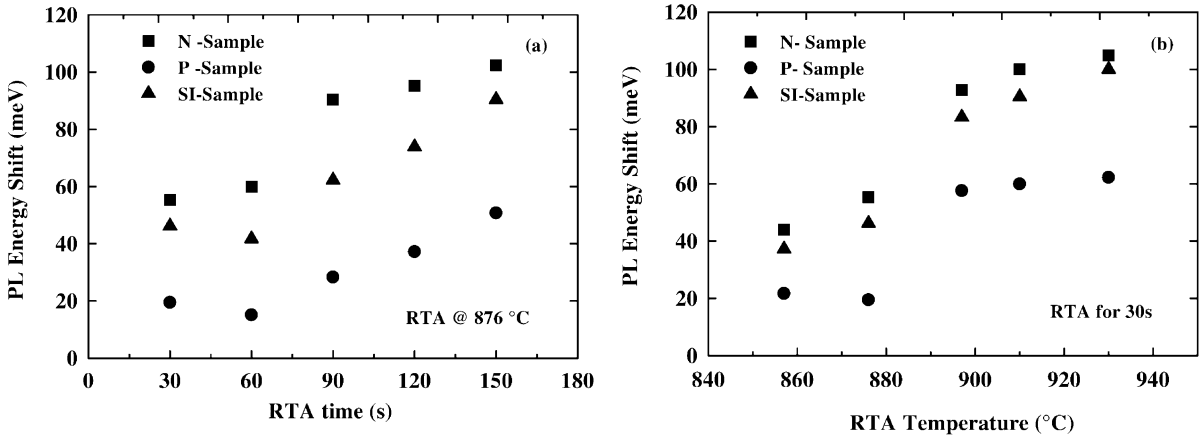

Fig. 2. PL energy shift relative to the as-grown samples for three samples: N-sample, P-sample, and SI-sample: (a) as a function of annealing time (annealing temperature, 876 °C); (b) as a function of annealing temperature (annealing time, 30 s). The experimental error was within ±5 meV.

sample almost saturates at temperatures above 900 °C, while for the SI-sample and N-sample the blue shift continues increasing with annealing temperature. The blue shift for these three samples is much larger than that observed in MOCVD-grown samples [8,19,20], likely due to the lower (580 °C) MBE growth temperature as compared to ~730 °C used in MOCVD growth in Yuan et al. [19]. In addition, there are other possible reasons: (a) trace impurities C and Zn are often present in MOCVD-grown samples as background doping when DMZn and CCl_4 are used as sources in the MOCVD system. Zn background doping can be as high as $\sim 5\times 10^{16}$ cm^{-3} [21], and may serve as the blocking Zn to reduce Group-III vacancies during the growth. (b) Carbon background doping may also play a role, but its diffusivity is much lower compared to Zn, so its effect may be negligible.

Most reports on Zn diffusion in III-V QW structures employ an external Zn source or an internal layer with heavy Zn-doping or by ion-implantation of Zn into the epitaxial layers [5,10,11]. In such works, Zn diffusion operates via interstitial-substitutional diffusion mechanism in most III–V semiconductors. Zinc atoms diffuse into the QW structure as charged interstitials and then move onto the group III sublattice to form immobile substitutional acceptors. Two mechanisms have been suggested for this [10]. In the first one, the interstitial Zn combines with a Ga vacancy to form the substitutional defect, and thus reduces the number of Ga vacancies. The second and slightly different mechanism is the 'kick-out' model. In this model, the Zn interstitials become substitutional acceptors by making the Ga atoms interstitial. The blue shift observed in the SI-Sample in this work is believed to be due to interdiffusion of Ga and Al atoms through Ga vacancies. The first mechanism causes a reduction in the number of Ga vacancies, and thus can reduce the blue shift of the QW structure. Krames et al. [13] have shown that by low temperature (480 °C) Zn 'blocking' diffusion from external $ZnAs_2$ source the Ga vacancy number and in turn the intermixing in GaAs/AlGaAs QW heterostructure was reduced. From our results, it is likely that at high temperature, more substitutional Zn atoms become interstitial Zn atoms, and diffuse into the $GaAs/Al_{0.24}Ga_{0.76}As$ QW structure and sit on the vacant Group III sites, therefore, reducing the Group III intermixing. Consequently, the blue shift in the PL measurements is reduced.

In order to determine the intermixing parameters, such as diffusion coefficient and activation energy, from the experimental data, we first calculate the sub-band energies and wave functions in the intermixing modified single non-square QW, and then compare the calculated interband transition energy to the PL data. The confinement profile of this intermixed QW is non-linear and is modeled here by an error function [22]. The diffused Al composition profile, $w(z)$, across the QW structure

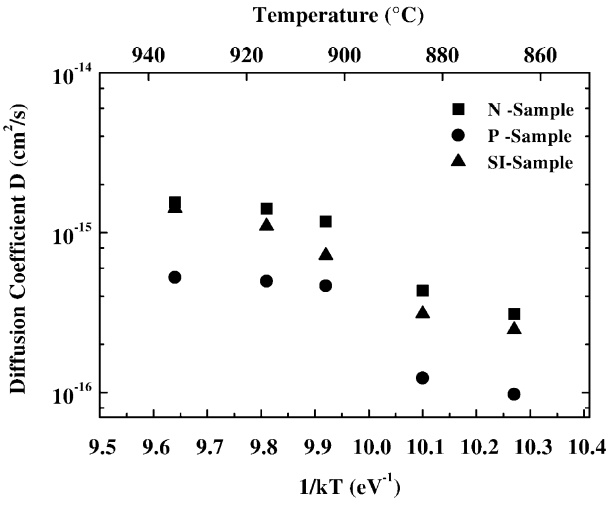

Fig. 3. Diffusion coefficient as a function of $1/kT$ for three samples: SI-sample, N-sample, and P-sample. The activation energy is 3.1 ± 0.1 eV, 2.9 ± 0.1 eV, and 3.2 ± 0.2 eV, for these samples, respectively. The experimental error was within ±5 meV.

is given by [23]:

$$w(z)=w_0\left\{1-\frac{1}{2}\left[\mathrm{erf}\left(\frac{L_z+2z}{4L_d}\right)+\mathrm{erf}\left(\frac{L_z-2z}{4L_d}\right)\right]\right\} \quad (1)$$

where w_0 is the as-grown Al mole fraction in the barrier, L_z is the as-grown width of the QW, z is both the quantization and the growth axis (QW centered at $z=0$), and erf denotes the error function.

The calculated QW interband excitonic transition energies are fitted to the measured energy shift of PL peak by adjusting the value of D. The diffusion coefficient D can also be expressed by the Arrhenius relationship:

$$D=D_0e^{-E_A/kT} \quad (2)$$

where D_0 is a prefactor, E_A is the activation energy, k is the Boltzmann constant, and T is the annealing temperature. D_0 and E_A are determined by a linear fit to the resulting values of $\ln(D/D_0)$ vs. $1/kT$. The Al profiles for various QWs are also calculated by the Eq. (1) using the fitted value of D.

The calculated diffusion coefficients for these three samples as a function of $1/kT$ are shown in Fig. 3. The data of SI-sample and N-sample is higher than that of P-sample. The activation energy for these three samples is 3.1 ± 0.1 eV, 2.9 ± 0.1 eV and 3.2 ± 0.2 eV, respectively. Taking into account the experimental error, these values are close to that of similar structures grown by MOCVD, which is approximately 3.2 eV [19], implying that the Ga–Al interdiffusion mechanisms were the same in both MBE-grown and MOCVD-grown samples, i.e. through the Group-III vacancy-mediated interdiffusion.

A possible mechanism of the improved thermal stability of GaAs/AlGaAs quantum well structures on Zn-doped GaAs substrate is discussed here. In this work, Zn was provided by Zn out-diffusion from the substrate. This Zn out-diffusion occurred during the growth, rather than the post-growth RTA process, as the Zn diffusion length during the short RTA was just a few nanometers as calculated below, and the GaAs buffer layer was 200 nm thick. We assume that Zn atoms (interstitials) diffused out of the substrate during the growth and moved forward with the growth front, and occupied some Group III-vacancies. The reduction of group III vacancies resulted in a reduction in the interdiffusion rate between Al and Ga in the quantum well region during the RTA processes, causing the improved thermal stability of the quantum well structure, which manifested itself in the reduced blue shift of the photoluminescence peak energy.

For all the three substrate wafers used in this work, namely semi-insulating GaAs, Zn-doped GaAs, and Si-doped GaAs, the main unintentional impurity was carbon. The background carbon concentration was approximately $3–5\times10^{14}$ cm^3, much lower than the Zn doping and Si doping of the p-type and n-type GaAs. Carbon diffusivity is orders of magnitude lower than that of Zn, for example, C the diffusion coefficient at 825 °C is $\sim1.0\times10^{-16}$ cm^2/s while that for Zn at 800 °C is $\sim6\times10^{-14}$ cm^2/s [24]. Therefore, possible effects of carbon in the substrate on the thermal stability of GaAs/AlGaAs quantum well structures might be neglected in the Zn-doped substrate. The concentration of other impurities should be even lower than C concentration in our samples and their effects on the thermal stability of the samples might also be neglected.

4. Summary

In conclusion, we have studied the effects of doping type in the GaAs substrate on the thermal stability in undoped GaAs/$Al_{0.24}Ga_{0.76}As$ single QW structures. The diffusion coefficient and activation energy were derived from the blue shift in the PL peak. It is found that Zn doping in the substrate reduces the Al-Ga interdiffusion in the QW. We believe this is likely due to the fact that Zn atoms diffused out from the substrate into the epitaxial layers and reduced the number of Group III vacancies, and thus reduced the Group III interdiffusion rate. The increased thermal stability can be applied to device processing directly to improve the performance and reliability of optoelectronic devices, HEMTs and HBTs.

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