InGaAsN/GaAs Quantum-well Laser Diodes

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Abstract - **GaAs-based InGaAsN/GaAs quantum well is found to be very sensitive to growth conditions and ex-situ annealing processes. Annealing could drastically increase the optical quality of GaAs-based InGaAsN/GaAs quantum well. As an end of this paper, some results on InGaAsN/GaAsN/AlGaAs laser diodes are also presented.**

Index Terms - **InGaAsN/GaAs, Quantum well, Molecular beam epitaxy, Laser Diode.**

I. INTRODUCTION

Semiconductor lasers emitting at 1.3μm and 1.55μm have been extensively employed in optical communication systems. The presently-used InGaAs/InGaAsP and InGaAsP/InP 1.3μm and 1.55μm lasers possess a relatively-poor characteristic temperature (T_0), typically ~60K[1]. Subsequently, temperature-control systems are compulsory for stable operation of these devices. While these devices have been long expected to operate stably over a wide temperature range without thermoelectric cooling, that requires a high characteristic temperature T_0. A novel material, InGaAsN/GaAs, has been proposed to solve this problem[2]. High conduction-band discontinuity of possibly more than 300meV at the interface of the III-(V,N)/III-V heterostructure has the potential of creating semiconductor lasers of high characteristic temperature T_0, for example, exceeding 150K[2]. The InGaAsN/GaAs laser diodes operating at 1.3μm and 1.55μm wavelength have been demonstrated, respectively[3][4]. Indeed recently, a T_0 value of 215 was demonstrated in GaInAsN/GaAs quantum well lasers emitting at 1.3μm[5]. Electrically-pumped vertical cavity surface emitting lasers (VCSELs) have also been reported[6].

Recent attempts have continuously been focused on growing GaAs-based nitrides of sufficiently high quality for the fabrication of laser diodes. However, the InGaAsN quality deteriorates dramatically with increasing nitrogen composition due to a large miscibility gap and phase separation, even though the amount of average strain in the epilayer anticipatorily decreases, as compared with the relevant InGaAs epilayer with the same indium composition. In an attempt of improving the material quality, a number of epitaxial techniques have been reportedly used for growing GaAs-based nitrides. These include metalorganic chemical vapor deposition (MOCVD)[7], molecular beam epitaxy

(MBE)[8] and metalorganic molecular beam epitaxy (MOMBE)[9]. It is often known that most nitrides are relatively stable at the growth temperatures in MOCVD due to the strong N-X bonds, hence making it difficult to incorporate nitrogen atoms into GaAs. Using the plasma-assisted MBE technique, a large nitrogen concentration in excess of 10%[10] has been successfully incorporated into the GaAsN materials. So far, the plasma-assisted MBE technique seems the best successful one for the growth of InGaAsN materials.

In this paper, we report our efforts to investigate the growth rules for GaAs-based nitrides towards 1.3μm laser diodes. Our results suggest that due to the occupation of interstitial sites by nitrogen atoms, annealing process become inevitable in device fabrication. Also presented are some laser diode results.

II. EXPERIMENTAL DETAILS

The laser structure was shown in Table I, and was grown in a SS-MBE system, equipped with five standard effusion cells for indium, gallium, aluminum, beryllium and silicon, three cracker cells for arsenic, phosphorous and hydrogen, and one plasma source for nitrogen, respectively. The purity of all the source charges is six nines. All samples were grown on (001)-oriented GaAs substrates

Table I: Sample Structure

GaAs(200nm)(Be,1×10^{19})
$Al_{0.4}Ga_{0.6}As$(1500nm)(Be,5×10^{17})
GaAs(150nm)
$In_{0.32}Ga_{0.68}As_{0.983}N_{0.017}$(7nm)
GaAs(40nm)
$In_{0.32}Ga_{0.68}As_{0.983}N_{0.017}$(7nm)
GaAs(40nm)
$In_{0.32}Ga_{0.68}As_{0.983}N_{0.017}$(7nm)
GaAs(40nm)
$Al_{0.4}Ga_{0.6}As$(1500nm)(Si,5×10^{17})
GaAs(500nm)(Si,1×10^{18})
GaAs substrate(Si,1×10^{18})

prepared using standard preparation procedures. Prior to growth, the surface oxide desorption was carried out under As_4 flux at a beam equivalent pressure (BEP) of 6.2×10^{-6} torr. A (2X4) surface reconstruction was maintained during the entire growth process. The beam equivalent pressures used for Ga and As were 4.5×10^{-7} torr and 6.2×10^{-6} torr, respectively, resulting in a growth rate of ~1.0 μ m/h which is verified by time resolved RHEED measurements. The nitrogen plasma source works at nitrogen background pressure of 3.6×10^{-6} torr in the presence of As_4 (6.2×10^{-6} torr) and is activated by radio frequency (R.F.) power greater than 60 W to maintain the plasma in high brightness mode.

The sample was annealed in a rapid thermal annealing (RTA) system with a 200nm thick SiO_2 protection layer deposited on the sample top. The RTA chamber was purged with an argon flow at a speed of 5 l/min for 5 minutes before the temperature was ramp up at a rate of 50 ^{o}C/s. The gas flow was then reduced to 2 l/min throughout the rest of RTA process. Temperature uniformity was maintained within ± 5°C across the a 4-inch area at the annealing temperature.

PL experiments were carried out using an optical system designed specially for compound semiconductors over a temperature range from 4.2K to 300K. Excitation was at near normal incidence using a 514.5nm beam from an Ar ion laser. The PL signals were collected with a dual grating spectrometer in the reflection direction and then detected using a liquid-nitrogen cooled germanium (Ge) detector in association with a standard lock-in technique.

An optimum RTA condition was identified with reference to RTA and PL measurements, and was applied to the fabrication of InGaAsN/GaAs lasers. 50μm wide photoresist stripes were first shaped with standard photolithography, the samples were then etched into 50μm wide mesas. With the photoresist strips still on the top of mesas, pulsed anodization was performed to form current blocking layer. The pulse voltage width was 1ms in a period of 12ms. The total anodization time was 6 minutes. The sample was then thinned to ~100 micron in thickness and Ti/Au and Au/Ge/Ni layers were deposited with electron beam evaporation on both sides for p-type and n-type ohmic contact. The sample was then diced into individual laser diodes with 600nm~1200micron cavity length. The uncoated lasers were tested on an indium probe stage with p-side down.

III. RESULTS AND DISCUSSION

Studying the RTA effects on InGaAsN/GaAs quantum well samples helps to find the optimum annealing conditions for luminescent efficiency, we therefore measured the PL spectra at 77K of as-grown and annealed InGaAsN/GaAs samples. Fig.1 shows the typical spectra of as-grown and annealed (670°C, 60sec) samples. The PL intensity increased significantly and the linewidth narrowed as well as compared with the as-grown sample, indicating that the radiation efficiency was improved noticeably by the annealing. The incorporation of nitrogen into InGaAs layer was proposed to introduce non-radiative centers.[11] Annealing may help to

reduce the non-radiative center density. The photon energy was also shifted to shorter wavelength. Fig.2 compares the integrated PL intensity as a function of annealing time at different RTA temperatures. The highest intensity can be reached at annealing temperatures between 650°C and 680°C for around 60 seconds. Pan et al[12] annealed their MBE-grown InGaAsN/GaAs quantum wells at 650°C for durations up to 30 minutes (much longer than in our case). They found that RTA generally improved the PL intensity and the longer the time the higher the PL intensity. They reported that for InGaAs/GaAs quantum well samples the PL intensity was insensitive to RTA annealing. They also annealed InGaAsN/GaAs samples at 900°C, and found that the PL intensity reached the maximum for 5 seconds annealing, then dropped with annealing time. Kageyama et al[13] annealed InGaAsN/GaAs quantum wells grown by chemical beam epitaxy for a fixed duration of 30 seconds and found that the maximum PL intensity was obtained at 675°C. Kagyame's InGaAsN quantum well had only 0.7% N, noticeably lower than 1.7% N in our laser structure. Their optimum RTA duration was somewhat shorter than ours (30 seconds versus 60 seconds). Xin et al[14], however, found that the maximum PL intensity was achieved at about 850°C for InGaAsN/GaAs quantum wells, much higher than our optimum temperature of about 670°C.
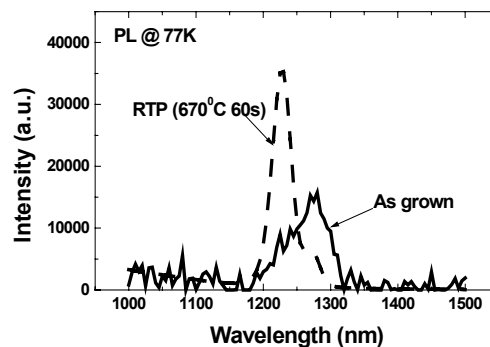

Fig.1 Typical PL spectra of as-grown and annealed InGaAsN/GaAs quantum well structures.
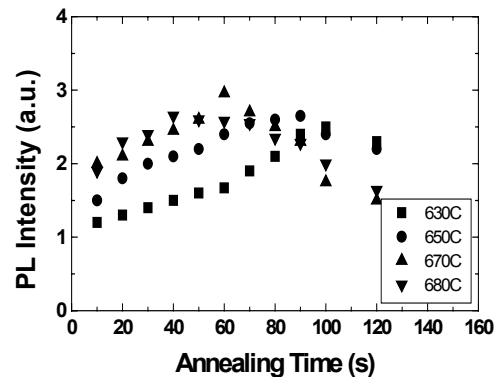

Fig.2 Integrated PL intensity as a function of annealing time at different annealing temperatures.

PL linewidth as measured with full width at half maximum (FWHM) is another important parameter for luminescent efficiency study. Fig.3 shows FWHM as a function of RTA time for different temperatures. It generally reaches minimum around 60 seconds for all the annealing temperatures, with the lowest value of 25 meV achieved by RTA at 670°C for 60 seconds, corresponding to the highest PL intensity as shown in Fig.2.
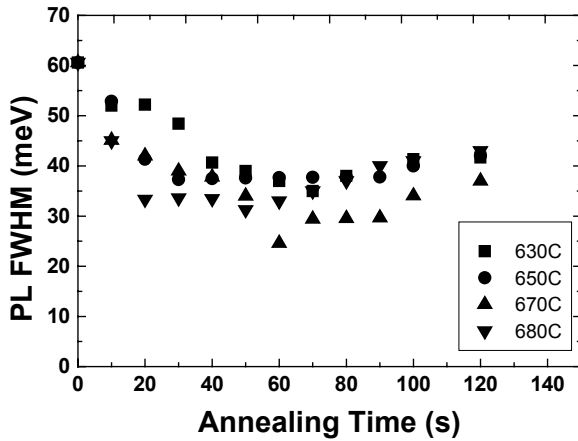

Fig.3 PL linewidth as a function of annealing time at different annealing temperatures.

The PL peak energy shifted following the RTA time towards higher energy as shown in Fig.4. At all temperatures, the blue shift was larger than 20meV even for the case of 10 second annealing. Yuan et al[15] recently did RTA annealing in InGaAs/GaAs quantum well samples at 825°C for 30 seconds and observed very little blue shift. The relatively large blueshift in this work might be due to two reasons: (1) the effect of SiO_2 encapsulation which was deposited onto the sample before rapid thermal annealing, and (2) the incorporation of nitrogen into InGaAs layers. SiO_2 is well know to enhance quantum well intermixing in InGaAs/GaAs[16] and GaAs/AlGaAs[17] quantum wells due to large diffusion coefficient of Ga in SiO_2, which increases Ga vacancies in GaAs that in turn enhances Ga and In interdiffusion. Similar effects were observed in GaNAs/GaAs quantum wells.[18] Burker et al[16] did RTA in InGaAs/GaAs with SiO_2 cap at temperatures higher than 850°C, showing a diffusion coefficient value of about $5 \times 10^{-17} cm^2/s$ at 700C for 15s. While in our case, the diffusion coefficient of indium (provided all the blue shift was due to indium diffusion) was determined as $3.4 \times 10^{-16} cm^2/s$ for the annealing at 680°C for 20s, much larger than the above estimation from Ref.16. Hence, SiO_2 cap alone can not account for the large blue shift observed in this work. Other part of blue shift is contributed by nitrogen diffusion. The blueshift increased steadily with RTA time from 0 to about 50seconds, and then flattened around 60seconds, and after ~80seconds it started to increase steadily again. The blue shift is an indicator of atom interdiffusion (i.e., In/Ga or N/As interdiffusion) in the quantum well, which is often enhanced by increasing Group-III vacancy density.[19] The flattening of blueshift increase following the annealing temperature for a 60sec duration (shown in Fig.4), as is coincident with the maximum PL intensity in Fig.2, indicating the vacancy density was minimized by RTA under that condition. Spruytte et al[11] found that as-grown samples contained a significant concentration of interstitial nitrogen that disappeared during a 1 minute annealing at 760°C. It is known that if the vacancies in the sample were occupied with other atoms, the vacancy number will be lower, and atomic interdiffusion process will be suppressed. For example, Zn diffused from p-type GaAs substrate into GaAs/AlGaAs quantum wells, taking up some vacancy sites in the quantum well, suppressing the Ga-Al atomic interdiffusion, reducing blue shift in the PL spectra.[20] If the interstitial nitrogen atoms in our samples had moved to occupy some of the vacancies during the annealing, especially at the optimum RTA point (i.e., 670°C for 60 seconds), the quantum well intermixing could be suppressed, resulting in the flattening of PL blueshift in Fig.4. It is possible that the reduction in vacancy number and nitrogen interstitials reduce the scattering of photogenerated carries in the PL measurement, leading to the reduction of the PL line width shown in Fig.3.
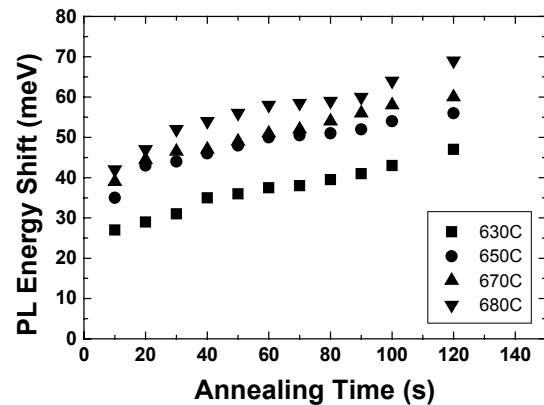

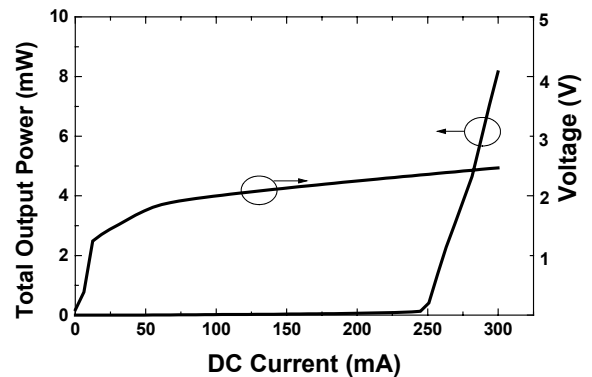Fig.4 PL peak shift with respect to annealing time at different annealing temperatures

Fig.5 Total light output power - current (L-I) and voltage-current (V-I) curves at 18K for a 50μmX1200μm laser diode.

Finding the optimum annealing condition, we annealed the laser structure at 670°C for 60 seconds, and then processed the wafer into lasers using pulsed anodic oxidation method. The lasers were tested in CW mode at 18K, and the optical and electrical characteristics are shown in Fig.5. Lasing was observed at currents above 250mA. Work is in progress to grow higher quality wafers. Fig.6 shows a typical laser emission spectrum at 50 K.
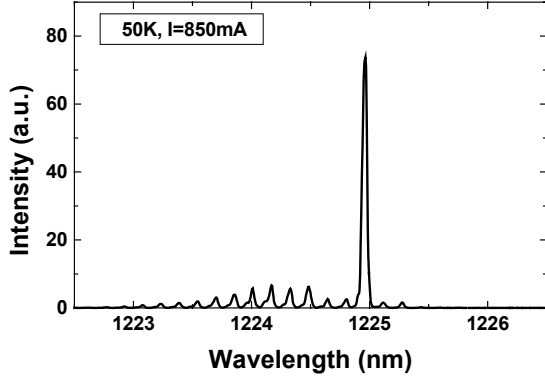

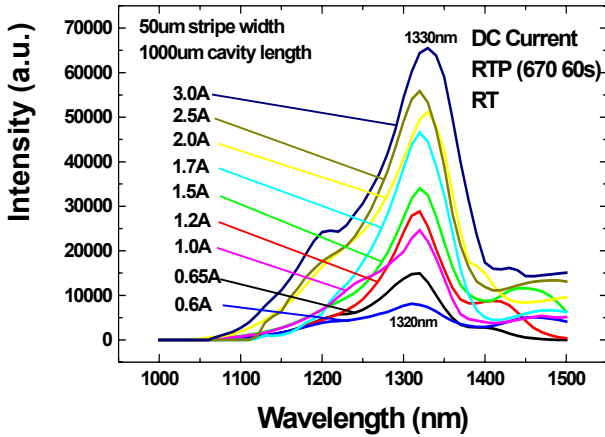Fig.6 Lasing spectrum at 50K for the same laser diode as is shown in Fig.5

Fig.7 EL spectra from laser diodes

The emitting wavelength is centered at 1.25μm at 50K. It could work in CW way at room temperature. The threshold current at room temperature is $1000 \sim 2500 A/cm^2$, which is comparable to literature listed in Table I. However, the light output L and dL/dI is three orders lower than the reported devices. It might be caused by large leakage current

Table I
Parameter comparison between our work with literatures. T for triple QW, D for double QW, and S for single QW structure.

	$I_{th}(A/cm^2)$	$dU/dI(\Omega)$	$dL/dI(W/A)$
This work	1120(T)	0.76	0.00028
Stanford	1500(T)	0.2	0.67
Finland	546(S)		0.28
Princeton	1320(S)		
Columbia	1020(S)		0.12
France	1220(S)		
Wisconsin	290(S)		
Hitachi	2860(S)		
Ricoh(Jap)	920(D)		

Although the laser diodes can operate at room temperature in cw mode, the threshold current at room temperature is relatively high that results in tremendous heat problem to the laser diodes. Even the indium probe stage is molten by the operating lasers, indicating the device temperature is at least higher than 165°C (indium melting point). That results in short lifetime of the devices, that can not sustain the lasing spectrum measurement at room temperature. Therefore, we measured the EL spectrum of these devices at low injection level though it is not lasing. The EL spectrum as shown in Fig.7 indicated that the emission peak is cantered at the right position of around 1320nm.

IV. SUMMARY

In summary, we have successfully fabricated InGaAsN/GaAsN/AlGaAs laser diodes emitting at 1320nm in cw mode at room temperature. Low light output warrants further optimization work on improving the material quality of quantum well region. There are three factors that may affect the quantum well quality: (1) growth interruption at the right quantum well interface of InGaAsN/GaAs, waiting for the ignition of nitrogen plasma source. (2) the InGaAsN surface is not perfectly smooth at the second interface of InGaAsN/GaAs quantum well. The long streaky RHEED patterns have been broken into short or very short lines, implying the roughness of the second quantum well interface. (3) the nitrogen content is somewhat too high, that may degrade the optical property of quantum well. Next growth run, we will try to grow the whole device structure without interruption and make sure the 2D growth mode of quantum well region. Optimum structure design will also help to reduce the injection level for lasing. We will make efforts to use narrower well and more indium in well region, both having the role to increase the energy separate between heavy hole (HH) and light hole (HH), and the ground energy level and the first energy level of heavy hole. That can ensure only the ground state of HH contribute to lasing, thus increase the gain factor and therefore reduce the threshold current.

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