Preliminary Results of InGaAsN/GaAs Quantum-well laser Diodes Emitting towards 1.3μm

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Abstract — GaAs-based nitride is found to be sensitive to growth conditions and ex-situ annealing processes. The critical thickness is almost one order thicker than the theoretical prediction by force balance model. The growth process could be sped up by the nitrogen incorporation itself, while the nitrogen incorporation could be affected by Beryllium doping. The incorporated nitrogen atoms partly occupy substitutional sites for Arsenic. Some nitrogen atoms are at interstitial sites. Annealing could drastically increase the optical quality of GaAs-based nitrides. As an end of this paper, some preliminary results of 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 are of fundamental importance in optical communication systems. The presently used InGaAs/InGaAsP and InGaAsP/InP 1.3μm and 1.55μm lasers have a poor characteristic temperature(T_0), with a typical value of ~60K[1], and subsequently cooling systems are needed. These devices have been long expected to operate stably over a wide temperature range without thermoelectric cooling, which requires a high characteristic temperature T_0. A novel material, InGaAsN/GaAs, has been proposed to solve this problem[2]. The 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 with high characteristic temperature T_0 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 148K 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 obtaining 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 increasing 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 used 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 article, we report our efforts to investigate the growth rules for GaAs-based nitrides towards 1.3μm laser diodes. Our results suggest that the critical thickness of GaAs-based nitrides is almost one order thicker than the theoretical prediction by force balance model. Growth process could be sped up by nitrogen incorporation, and even doping could affect the nitrogen composition in GaAsN. Due to the occupation of interstitial sites by nitrogen atoms, annealing process become inevitable in device fabrication.

II. EXPERIMENTAL DETAILS

The GaAsN and InGaAsN samples were 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 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 $6.2X10^{-6}$ torr. A (2X4) surface reconstruction was maintained during the entire growth process. The beam equivalent pressures used for Ga and As were $4.5X10^{-7}$ torr and $6.2X10^{-6}$ torr, respectively. The V/III ratio was fixed at about 14 for the growth of all samples. The Ga and As fluxes were adjusted by controlling the temperature of the effusion cells. The above BEPs result in a growth rate of ~1.0 μm/h which is verified by time resolved RHEED measurements. The nitrogen plasma source works at nitrogen background pressure of $3.6X10^{-6}$ torr in the presence of As_4 ($6.2X10^{-6}$ torr) and is activated by radio frequency (R.F.) power greater than 60 W to maintain the plasma in high brightness mode.

A GaAs buffer layer was first grown onto the GaAs substrate at 590°C. The substrate temperature was then reduced to the desired value of 460°C for growth of the following individual GaAsN/GaAs, InGaAsN/GaAs structures and their combined structures. XRD measurements were carried out on the samples, and 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.

III. RESULTS AND DISCUSSION

Figure 1 shows a relationship between the nitrogen composition in GaAsN and the r.f.power applied to nitrogen plasma source, while the thickness of all the GaAsN samples is controlled to be 90nm. The open circles are experimental data, and the solid line is for eye guidance. The nitrogen composition in GaAsN increases linearly with the increasing r.f.power up to 220W, under the conditions indicated in figure 1. The anticipating nitrogen composition will be around 3.45% shown with a solid circle, if the sample goes along the nitrogen-increasing trend. But the experimental result deviates the nitrogen–increasing trend largely, presenting a nitrogen value much lower than the anticipated. This phenomenon suggests that this sample has most probably undergone certain physical transformations. Thickness-related XRD measurements[11] indicate that as the nitrogen composition increases with the r.f.power applied to nitrogen plasma source, the sample at 240W reached its critical thickness and relaxed. This is in good accordance with the RHEED pattern observations showing a spotty pattern at the growth end of this sample. Compared with strained samples, a relaxed sample causes its XRD peak shifting towards the substrate peak, resulting in a drop in nitrogen composition of GaAsN when the strained simulation program is continuously performed. With comparison with the Matthews-Blakeslee force balance single-kink model for the critical thickness h_c of epilayer which is given by[11][12]

$$h_c = \left(\frac{b}{4\pi f}\right)\left(\frac{1-\nu/4}{1+\nu}\right)\left(\ln\left(\frac{h_c}{b}\right)+1\right) \quad (1)$$

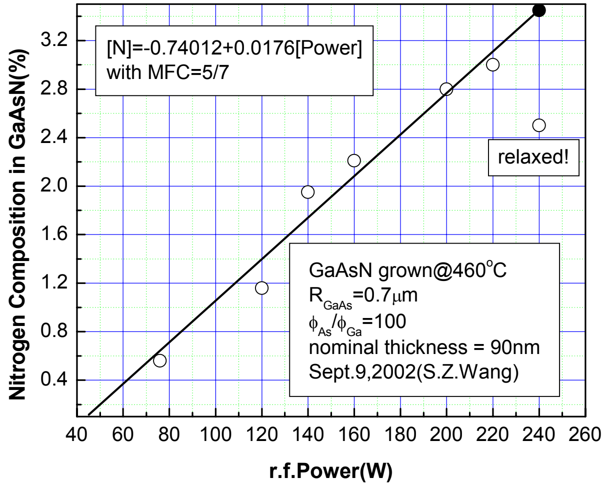


Fig.1 Nitrogen composition in GaAsN is shown as a function of r.f.Power applied to nitrogen plasma source. All GaAsN samples are controlled in the same thickness of 90nm.

where Poisson's ratio ν, Burger's vector b of dislocation and misfit strain f are functions of the nitrogen composition. The critical thickness calculation for the GaAsN with 3.45% of nitrogen shows that our measured critical thickness for GaAsN is around 5 times thicker than the theoretical prediction. However, the deviation between our measured value and the theoretical result is in rough accordance with the comparison in ref.[11] between theoretical calculations and experimental results. This suggests that the GaAsN material is as common as InGaAs material with respect to critical thickness.

Figure 2 shows the thickness of GaAsN samples with same growth times as a function of nitrogen composition. The solid circles, open circles and open triangle indicate experimental data, while the solid line is guidance for eye. This diagram tells that although the growth time for all those GaAsN samples is same, the thickness of these samples with different nitrogen content is different. This implies that the growth rate of GaAsN material could be affected by the presence of nitrogen, showing that the growth rate of GaAsN increases linearly following its increasing nitrogen composition. This is true till the point that is denoted by the open triangle at around 2.8% nitrogen. Following the increasing trend of growth rate with nitrogen composition, the thickness of the sample of 2.8% nitrogen should locate in the solid line, however the measured thickness of this sample is higher than what the trend could predict. This is

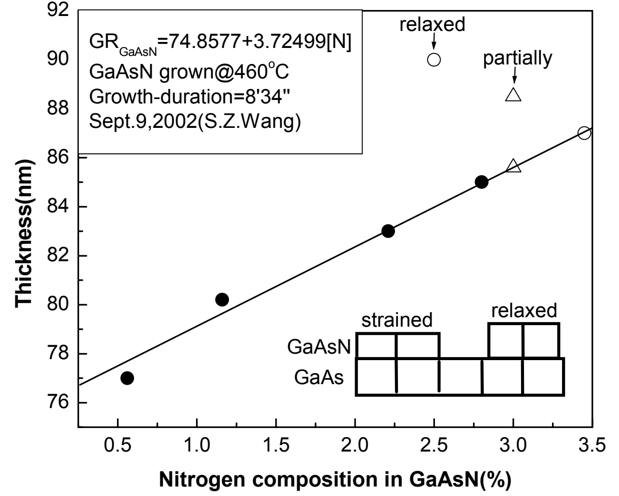


Fig.2 Thickness of GaAsN samples is plotted against their nitrogen compositions

because this sample is partially relaxed. In the previous paragraph, the mechanism how the relaxation could effect the simulation result of nitrogen composition in GaAsN sample has been discussed. Here we focus our attention on how the sample thickness is changed by the relaxation.

The unit volume V_{GaAsN} of GaAsN alloy could be expressed by

$$V_{GaAsN} = a_{\perp} \cdot a_{//} \cdot a_{//} \qquad (2)$$

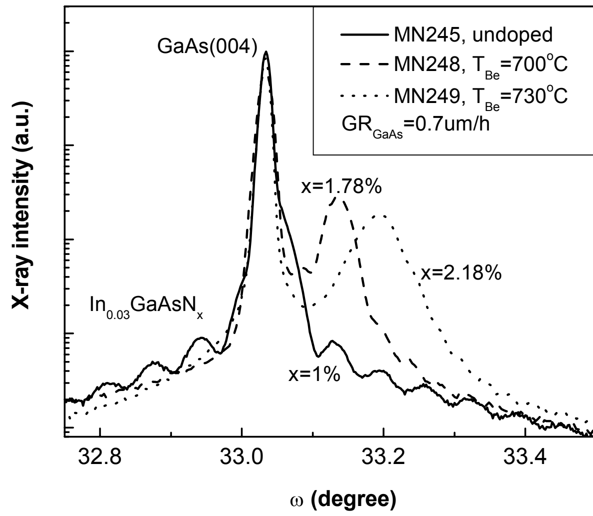
where $a_{\perp}$ and $a_{//}$ are lattice constants perpendicular and parallel to the GaAs substrate surface, respectively. Therefore, the lattice constant perpendicular to GaAs substrate surface is got as

$$a_{\perp} = V_{GaAsN}/ a_{//}^{2} \qquad (3)$$

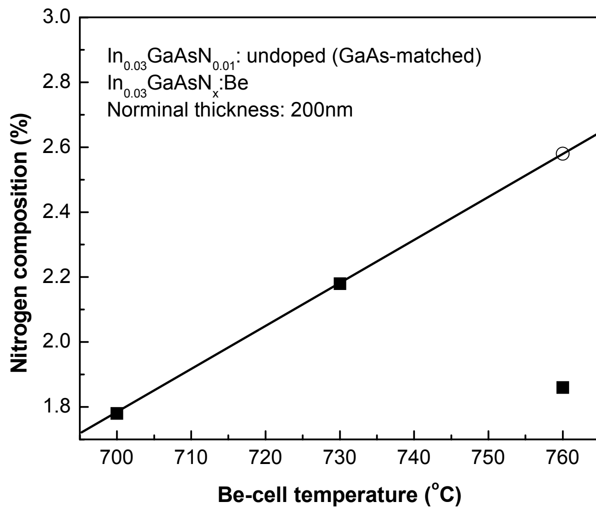
and the thickness d_{GaAsN} of GaAsN material could be expressed by

$$d_{GaAsN} = \sum_{i=0}^{n} a_{\perp} \qquad (4)$$

n denotes the total sum of unit cell perpendicular to substrate surface.



(a)



(b)

Fig.3 (a) A batch of XRD spectra from InGaAsN samples with different doping levels; (b) A relationship between nitrogen composition in InGaAsN and Be-cell temperature.

It is commonly known that the radius of nitrogen atom is much smaller than either gallium atom or arsenic atom. Therefore, if nitrogen atom substitutes for some arsenic sites in GaAs material to form GaAsN alloy, the lattice constant of GaAsN alloy would be smaller than that of GaAs substrate, as is schemed in the inset of Fig.2 for relaxed GaAsN. When GaAsN is pseudo-morphologically grown on GaAs substrate, the GaAsN lattice parallel to substrate surface is forced to equalize GaAs lattice, resulting in the stretch of $a_{//}$. According to Eq.(3), $a_{\perp}$ would be contemporarily shortened. That is the situation as is schemed in the inset of Fig.2 for strained GaAsN. Relaxation has a reverse function on the lattice constant of GaAsN epilayer, on the other hand. With increase of nitrogen composition in Fig.2, the thickness of GaAsN epilayer increases in good linearity till the points denoted by open-triangle and open-circle marks, at which the GaAsN samples are known to be partially relaxed and fully relaxed respectively through the RHEED pattern observations. As the relaxation happened at the open-triangle point and open-circle point, the $a_{\perp}$ was suddenly enlarged at the moment the relaxation was happening and the epilayer thickness was consequently increased through Eq.(4).

Figure 3(a) shows a batch of XRD spectra from $In_{0.03}Ga_{0.97}As_{1-x}N_x$ samples with different Beryllium doping levels. The solid curve is from a nominally undoped $In_{0.03}Ga_{0.97}As_{0.99}N_{0.01}$, showing that this sample is exactly GaAs-matched with smooth interface between GaAs substrate and $In_{0.03}Ga_{0.97}As_{0.99}N_{0.01}$ indicated by the presence of strong fringes. This sample when doped with Beryllium shows one more XRD peak in the right side of GaAs substrate peak. This phenomenon has never been found, to the best of my knowledge, in InGaAs and GaAs materials, suggesting that the nitrogen incorporation behavior might be enhanced by Beryllium doping. Higher Beryllium doping level results in higher nitrogen composition. However, with the increase in nitrogen composition, the relevant XRD spectrum shows fewer fringes and broader peaks, indicating the crystal quality deteriorated. Experimentally, when the doping level increases further, for example, to T_{Be}=760°C, the InGaAsN sample relaxed, as is judged by the presence of spotty RHEED pattern. Figure 3(b) shows a relationship between the nitrogen composition in InGaAsN and Be-cell temperature. The solid squares are experimental data with the solid line for eye guidance. As the Be-cell temperature increase, the nitrogen composition in InGaAsN is increased. When the Be-cell

temperature is raised up to 760°C, the anticipated nitrogen composition will be around 2.6%, however the measured nitrogen value is only 1.85%. This is a characteristic behavior of relaxation, as is discussed in Figure 1.

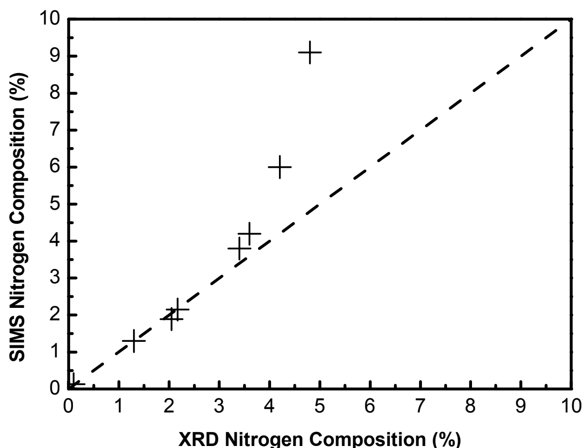
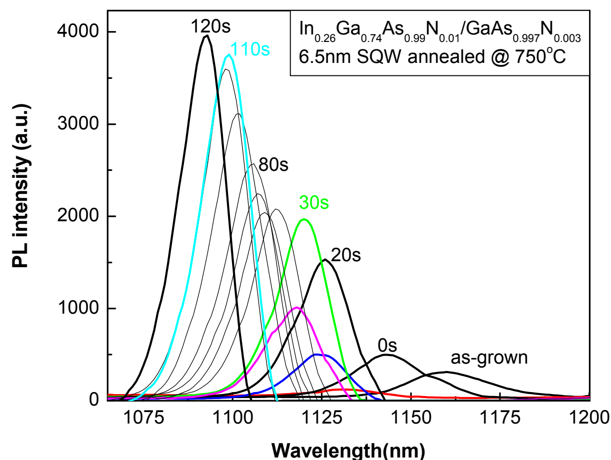
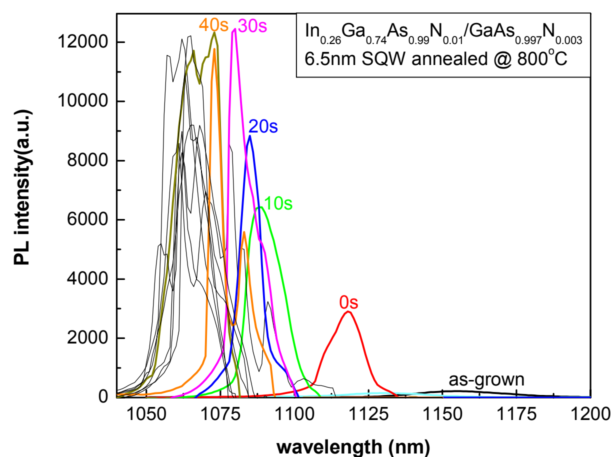


Fig.4 A comparison of nitrogen composition in GaAsN measured with SIMs and XRD simulation

Figure 4 presents a comparison of nitrogen composition in GaAsN measured with SIMs and XRD simulation. The cross marks are experimental data, and the dashed line expresses the equalization of nitrogen composition obtained with the two methods. The two methods could be identical with each other as the nitrogen composition in GaAsN is lower than around 2%. But when the nitrogen composition in GaAsN is higher than 2%, the nitrogen composition results obtained from SIMs method become higher than that measured with XRD simulation. The higher the nitrogen composition in GaAsN, the larger the deviation between the data acquired with these two methods. According the measurement principle, XRD calculates the nitrogen composition in GaAsN from the separation between GaAsN peak and GaAs substrate peak. Therefore, only those nitrogen atoms that induce the change of lattice constant of matrix could be examined by XRD. Those nitrogen atoms that do not affect the lattice constant would not be included. While SIMs measurement could account all the nitrogen atoms in GaAsN material regardless of the different roles they might play in GaAsN. Therefore, it is reasonable that the measured nitrogen composition with SIMs is probably higher than that with XRD simulation. In fact, the nitrogen atoms in interstitial sites would not cause the expansion or shrinkage of GaAs lattice due to its much smaller volume than the host atoms of gallium and arsenic. The interstitial nitrogen atoms as well as other defects could deteriorate the optical property of nitride materials and could be removed through thermal annealing method.



(a)



(b)

Fig.5 The PL spectra from InGaAsN/GaAsN QW samples annealed at 750°C (a) and 800°C for different annealing times.

Figure 5(a) shows a batch of PL spectra from InGaAsN/GaAsN single quantum well sample at 5K, which is subject to an annealing process at 750 degree for different times. The outstanding characteristics of these PL spectra is the blue shift of the PL peak from around 1160nm to 1090nm and the drastic increase in PL intensity of more than 25 times higher than that of as-grown sample. But the lineshape and FWHM of the PL peak remain almost unchanged. Fig.5(b) presents some PL spectra from the same InGaAsN/GaAsN single quantum well sample at 5K, which underwent an annealing process at 800 degree for different times. Besides the blue shift of the PL peak, the PL intensity is enhanced up to 58 times higher than that of the as-grown sample. This is much stronger than that from samples annealed at 750 degree, implying that most of the intensity-related defects could be removed with 750 degree annealing, but other defects could only be removed by annealing under higher temperatures. That suggests that some defects are of smaller activation energy, while others are of higher thermal activation energy. The FWHM of the PL peak could be changed with the annealing at 800 degree. That is, the FWHM-related defects are of higher thermal activation energy. The higher thermal activation energy could reduce the FWHM of PL peak. However, it is also noticed that over-annealing may deteriorate the sample quality. Because the PL spectra show the presence of multi-peak and broadening of PL peak as well. This gives an impression that cares should be taken when nitride samples are being annealed, since for a complicated system it is not equivalent to anneal at low temperature for long time and to anneal at high temperature for short time.

After annealing, a laser diode has been fabricated successfully using InGaAsN/GaAsN/AlGaAs structure. The stripe width is 50μm, and cavity length is 1000μm. The L-I and I-V curves of an uncoated and uncooled laser diode are shown in Fig.6. The emitting wavelength is centered at 1.15μm. It could work in CW way at room temperature. The threshold current value is 1000~2500A/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

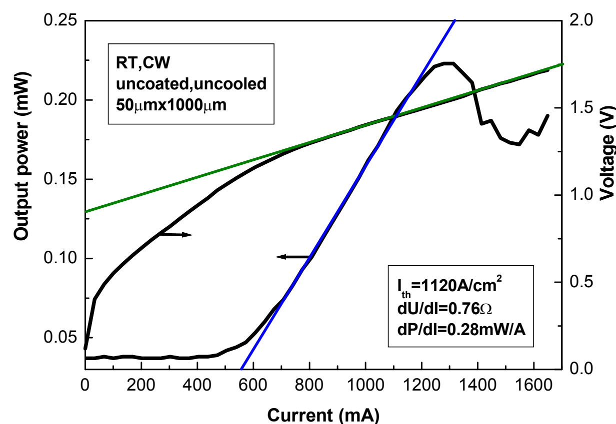


Fig.6 L-I and I-V curves of an InGaAsN/GaAsN triple quantum well laser diode.

Fig.7 An infrared near-field pattern of an InGaAsN/GaAsN triple quantum well laser diode.

due to weak carrier confinement and high EPD of the used GaAs substrate, which is two orders higher than the substrate commonly used for laser fabrication. Fig.7 is the near-field pattern taken with a silicon-based CCD array.

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(Ω)	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)		

IV. SUMMARY

In summary, the GaAs-based nitride is found to be sensitive to growth conditions and ex-situ annealing processes. The critical thickness is almost one order thicker than the theoretical prediction by force balance model. The growth process could be sped up by the nitrogen incorporation itself, while the nitrogen incorporation could be affected by Beryllium doping. The incorporated nitrogen atoms partly occupy substitutional sites for Arsenic. Some nitrogen atoms are at interstitial sites. Annealing could drastically increase the optical quality of GaAs-based nitrides. As an end of this paper, some preliminary results of InGaAsN/GaAsN/AlGaAs laser diodes are also presented. Low light output warrants further optimization work on this device.

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