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Improved GaN_xAs_{1-x} quality grown by molecular beam epitaxy with dispersive nitrogen source

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A modified mode for GaAsN growth using solid-source molecular beam epitaxy in conjunction with dispersive nitrogen to avoid the bombardment effect of energetic nitrogen ions is reported. High-quality GaAsN epilayers and good GaAsN/GaAs interfaces were achieved using this growth mode. The results suggest that the surface of samples grown using dispersive nitrogen has fewer defects than those grown using the direct nitrogen beam. The optical quality of GaAsN samples grown using the dispersive nitrogen technique was found to improve, due to the lower nitrogen ion bombardment effect. This growth technique is expected to be advantageous for growing high-quality GaAsN materials for optoelectronic applications. © 2002 American Vacuum Society. [DOI: 10.1116/1.1490391]

I. INTRODUCTION

The increasing demand for 1.3 and 1.55 μm optical communication systems and networks paves the way for the development of new material systems such as GaAs-based nitrides. This material system, when grown on a GaAs substrate, offers the strong possibility of making devices that are able to operate at such wavelengths due to the large band gap bowing effect. Laser diodes operating at a 1.3 μm wavelength based on the quaternary GaInAsN on GaAs substrate have been demonstrated.¹ The use of GaAs-based GaInAsN and GaAsSbN materials for potential applications in a 1.55 μm laser diode application has also been reported.² The high conduction band discontinuity of possibly more than 300 meV at the interface of the III-(V,N)/III-V heterostructure³ has the potential for creating semiconductor lasers with a high characteristic temperature T_0 exceeding 150 K. Indeed, recently a T_0 value of 148 K was demonstrated in GaInAsN/GaAs quantum well lasers emitting at 1.3 μm .⁴

Recent attempts have been focused on obtaining GaAs-based nitrides of sufficiently high quality for the fabrication of laser diodes. A number of epitaxial techniques have reportedly been used for growing GaAsN. These techniques include metalorganic chemical vapor deposition (MOCVD),⁵ molecular beam epitaxy (MBE),⁶ and metalorganic (MBE).⁷ It is 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%⁸ has been successfully incorporated into the GaAsN materials. However, the layer quality is far from the requirement for device fabrication and could be susceptible to degradation due to the presence of energetic nitrogen ions, resulting in poor optical properties.

To minimize the bombardment effect of energetic nitrogen ions, the GaAsN materials in our study were grown using the dispersive plasma-activated nitrogen technique in a solid-source MBE (SSMBE) system. Compared to the conventional MBE and MOCVD technique, this is a modified growth method. Double-crystal x-ray diffraction (XRD) and photoluminescence (PL) measurements, as well as the observation of a clear (2 \times 4) streaky reflection high-energy electron diffraction (RHEED) pattern, indicate that the samples have high crystalline and optical quality and a good interface.

II. EXPERIMENTAL DETAILS

The GaAsN samples were grown in a SSMBE system. This system was 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 semi-insulating GaAs substrates that were prepared using standard preparation procedures. A (2 \times 4) surface reconstruction was maintained during the entire growth process. The beam equivalent pressures used for Ga and As were 4.5×10^{-7} and 6.2×10^{-6} Torr, respectively. The V/III ratio was fixed at about 14 for the growth of all samples. The above beam-equivalent pressures result in a growth rate of ~ 1.0 m/h verified by time-resolved RHEED measurements and a step profiler. The nitrogen plasma source works at a nitrogen background pressure of 3.6×10^{-6} Torr in the presence of As₄ (6.2×10^{-6} Torr) and was activated by radio frequency (rf) power greater than 60 W to maintain the plasma in high brightness mode.

An undoped GaAs buffer layer of ~ 300 nm 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 GaAsN epilayer. The GaAsN sample employed here was ~ 100 nm in thickness, with a GaAs cap layer of 20 nm. XRD measurements were carried out on the

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samples. PL experiments were carried out at 4 K. Using a 514.5 nm beam from an argon ion laser, excitation was at near normal incidence. The PL signals were detected using a liquid-nitrogen cooled germanium (Ge) detector in association with a standard lock-in technique.

III. RESULTS AND DISCUSSION

The fundamental characteristic of conventional MBE growth depends on the material fluxes, which are supplied directly to the growth surface. Under such conditions, dynamic processes on the growth surface govern the growth characteristics. In our experiment, the growth of GaAsN uses a conventional gallium-effusion cell and a cracker cell for arsenic. A rf activated plasma source is used to generate the nitrogen species. A shutter is inserted into the path of the nitrogen beam in order to interrupt the energetic nitrogen ions and prevent them from bombarding directly onto the growth surface. Hence, the nitrogen species are supplied to the growth surface in a dispersive manner, using the background pressure in the growth chamber as an indicator. Because the shutter is also utilized as a cooled shield for the plasma source, the energetic species generated by the plasma source can be reduced to lower energy states when the species impinge onto the cooled shutter.

Because the shutter is electrically grounded, positively or negatively charged plasma products can be neutralized. Behaving as a kind of energy attenuation and charge filter, the cooled and grounded shutter enables the supply of neutralized nitrogen radicals to the growth surface. This has been confirmed by quadrupole mass spectrometer measurements of the nitrogen radicals and results from material growth experiments to be discussed later in this article.

For our MBE system configuration, the optimal background nitrogen pressure for effective operation of the plasma source is $\sim 3.4 \times 10^{-6}$ Torr. All samples reported herein were grown under this optimal pressure condition. Figure 1 shows the relationship between the nitrogen composition in the GaAsN epilayers and the rf power applied to the plasma source. The nitrogen composition was determined by fitting the dynamical theory to the XRD experimental data. Our experiments reveal that the nitrides can be grown with either a direct nitrogen beam from the plasma source or dispersive nitrogen from the background. In Fig. 1, the solid diamond symbols indicate the nitrogen composition in GaAsN grown with direct nitrogen beam from the plasma source, while the solid dot symbols denote the corresponding nitrogen composition in GaAsN epilayers grown with dispersive nitrogen source.

It is noted that regardless of whether the growth was carried out with a direct nitrogen beam or a dispersive nitrogen source, the nitrogen composition in the GaAsN epilayer increases monotonously as the rf power increases. Our measurements revealed that the nitrogen flux from the direct nitrogen beam is $\sim 2.0 \times 10^{-7}$ Torr. Therefore, the solid diamond symbols represent the combined data caused by the direct nitrogen beam and background active nitrogen in the chamber.

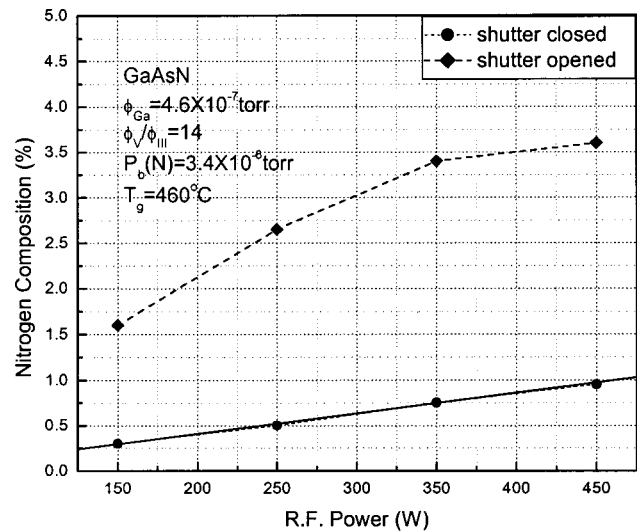


FIG. 1. Experimental and fitting results of nitrogen composition in GaAsN layer vs rf power of the nitrogen plasma source, under the conditions indicated: (♦) nitrogen composition in GaAsN grown with direct nitrogen beam, (•) nitrogen composition in GaAsN epilayers grown with dispersive nitrogen source.

The solid line fitted through the dot symbols was obtained by assuming the number of active nitrogen species in the background is a linear function of the rf power. The excellent agreement between the fitted line and experimental data indicates that the assumption of a linear relationship between the active nitrogen concentration and rf power is reasonable.⁹

On the other hand, the nitrogen composition in the GaAsN epilayer grown with a direct nitrogen beam exhibits a superlinear behavior following the increase in rf power, suggesting a saturation behavior in nitrogen incorporation. Because the nitrogen composition in the material contributed by dispersive nitrogen does not show any deviation from linearity, the saturation behavior in nitrogen incorporation in material grown using a direct nitrogen beam can possibly be attributed to the saturation of activated nitrogen flux emitting from the plasma source, due to a decrease of the rf power coupling factor. This explanation is reasonable, because the nitrogen within the plasma source has pressure as low as 10^{-2} – 10^{-4} Torr, and there is a limit to how much the rf power can be coupled to the nitrogen gas.

Figure 2 shows two XRD rocking curves of the GaAsN layers at the (004) diffraction direction. The solid curve is data from the sample grown with the dispersive nitrogen source. The dashed curve is data from the sample grown using the direct nitrogen beam. With reference to the GaAs substrate peak, the GaAsN peak is easily identifiable, and the nitrogen composition deduced from the simulation result is $\sim 1.3\%$. This is in good agreement with the nitrogen composition result of $\sim 1.3\%$ deduced from the secondary ion mass spectroscopy measurement. Consistent with the RHEED pattern observations, the strong XRD peak further testifies to the high quality of the GaAsN epilayer. Strong fringes are also observed in both XRD spectra, indicating the presence of a smooth and abrupt GaAsN/GaAs interface. The XRD

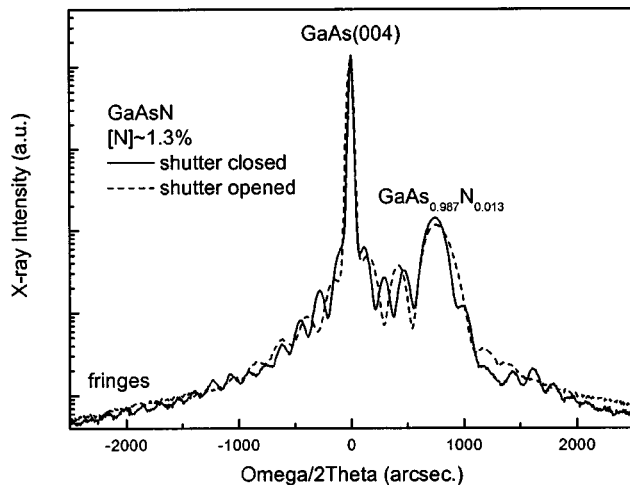


FIG. 2. XRD rocking curve of the as-grown GaAsN epilayer in the (004) diffraction direction. The solid curve is data from the sample grown with a dispersive nitrogen source, and the dashed curve is data from the sample grown using a direct nitrogen beam.

result of our sample grown with a dispersive nitrogen source has a smaller full width at half-maximum (FWHM) value compared to that reported by Harmand *et al.*,¹⁰ whose samples have nitrogen composition of $\sim 1.1\%$ to $\sim 1.2\%$.

In addition to the fact that the XRD peak of the sample grown with the dispersive nitrogen source is stronger than that of the sample grown with the direct nitrogen beam, the FWHM of the XRD peak of the sample grown with dispersive nitrogen source is also narrower than that of the sample grown using the direct nitrogen beam (195 versus 251 arcsec). This clearly indicates higher crystalline quality in the sample grown with the dispersive nitrogen source compared to the sample grown using the direct nitrogen beam, as is presented in Table I, which shows a comparison of six samples grown under direct nitrogen beam and dispersive nitrogen. Furthermore, the sample grown with the dispersive nitrogen source has more fringes in the XRD spectrum, indicating the presence of a smoother and more abrupt interface between the GaAsN and GaAs layers.

In an rf activated direct nitrogen beam process, the nitrogen species include N atoms, N^+ and N_2^+ ions, and metastable N^* atoms and N_2^* molecules in the excited states.^{11,12} The excited molecular species, such as N_2^+ and N_2^* , are the effective reactive species. Due to difficulty in breaking the extremely strong N–N chemical bonds at the low substrate

temperature in MBE growth, these species are readily incorporated into the material to form clusters. Thus, both the crystalline and interface quality of the material can be degraded by the presence of N_2^+ and N_2^* reactive species.

This is the reason why the sample grown with the direct nitrogen beam has a broader XRD peak and fewer fringes in the spectrum. In the case of the dispersive nitrogen source, the N_2^+ ions are neutralized, and the N_2^* molecules are relaxed to the ground state to form N_2 molecules. These N_2 molecules then become part of the N_2 background, which does not participate in the growth process. The advantages of using the dispersive nitrogen source in MBE growth of GaAsN are further corroborated by the following experimental evidence.

Figure 3 shows two PL spectra of the GaAsN epilayers at 4 K. The solid curve is the data from the sample grown with a dispersive nitrogen source, and the dashed curve is the data from the sample grown using a direct nitrogen beam. The PL peaks of both spectra, which are located at ~ 1034 nm (~ 1.2 eV), are consistent with the XRD results. It is noted that the PL peak of the sample grown with the dispersive nitrogen source is much stronger than that of the sample grown with the direct nitrogen beam.

Furthermore, the FWHM of the PL peak of the sample grown with the dispersive nitrogen source is as narrow as 42.4 meV. This is significantly smaller than that of the sample grown with the direct nitrogen beam of 99.2 meV, indicating the higher crystalline quality in the sample grown with the dispersive nitrogen source, as is shown in Table I. Moreover, the sample grown with the direct nitrogen beam has a prominent low-energy tail in the PL spectrum, the reason for which is unclear at this moment.

Li *et al.*¹³ have attributed the poor optical properties of their as-grown samples to several possible reasons, such as implantation damage, presence of group-V vacancies, and impurities. In the case of our samples, the growth conditions are essentially the same, except for the manner in which the nitrogen is introduced (dispersive versus direct nitrogen beam). Hence, this suggests that the concentration of group-V vacancies and impurities is essentially the same. However, because the PL properties of the samples grown using the dispersive nitrogen source and the direct nitrogen beam are quite different, the group-V vacancies and impurities could not be the main mechanism responsible for the poor optical property of the material.

Therefore, it is highly probable in our case that the use of

TABLE I. Comparison of sample properties grown under direct nitrogen beam and dispersive nitrogen.

Nitrogen composition and growth mode		XRD FWHM (arcsec)	PL FWHM (meV)	Defect density (/cm ²)
0.6%	Dispersive	169	35.6	$\sim 5.4 \times 10^3$
	Direct beam	201	66.3	$\sim 6.7 \times 10^4$
1.0%	Dispersive	178	37.8	$\sim 7.8 \times 10^3$
	Direct beam	223	78.6	$\sim 8.6 \times 10^4$
1.3%	Dispersive	195	42.4	$\sim 1.0 \times 10^4$
	Direct beam	251	99.2	$\sim 1.0 \times 10^5$

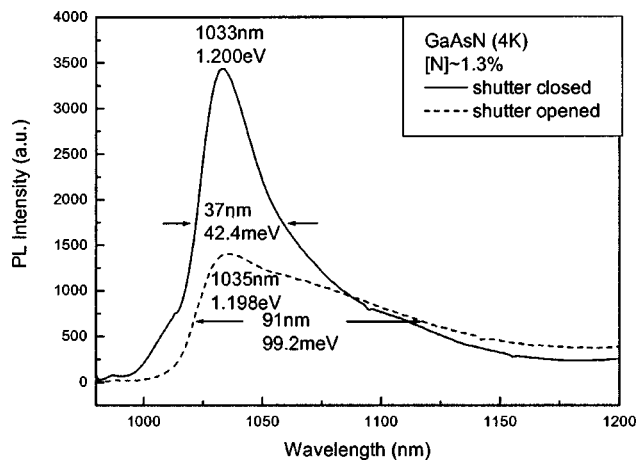


FIG. 3. Low temperature (4 K) PL spectra of as-grown GaAsN epilayers. The solid curve is data from the sample grown with a dispersive nitrogen source, and the dashed curve is data from the sample grown using a direct nitrogen beam.

the dispersive nitrogen mode during growth has significantly reduced the effects of implantation damage due to the energetic nitrogen ions, hence improving the optical quality of the sample. Although the low-energy tail in the PL spectrum has been suppressed by use of the dispersive nitrogen mode, the PL peak of GaAsN is not as narrow as expected. The reasons for the broadening and presence of the low-energy tail in the PL spectrum, and ways to improve the optical property of the material, warrant further investigation of the growth mechanism. Because the PL measurement was performed at 4 K, it is probable that the PL emission comes from the radiative recombination of excitons in the unintentionally doped GaAsN material, and the low-energy emission arises from the defect-related mid-gap energy levels.

Figure 4 compares two typical light microscopy pictures of the GaAsN surface of samples grown using: (a) the dispersive nitrogen growth mode and (b) the direct nitrogen beam growth mode. This preliminary comparison shows that the GaAsN sample grown using dispersive nitrogen has fewer defects on the surface than the sample grown with the direct nitrogen beam from the plasma-activated nitrogen source. In fact, from our experience, it is rather difficult to find a view spot with several defects on the surface of the GaAsN sample grown using dispersive nitrogen. On the contrary, there are many defects on the surface of the GaAsN sample grown using the direct nitrogen beam. Some values of the defect density in samples grown using the direct nitrogen beam and dispersive nitrogen are indicated in Table I. It is unclear whether the reduced number of surface defects on the sample grown using dispersive nitrogen was due to the lower bombardment effect of energetic nitrogen ions, an

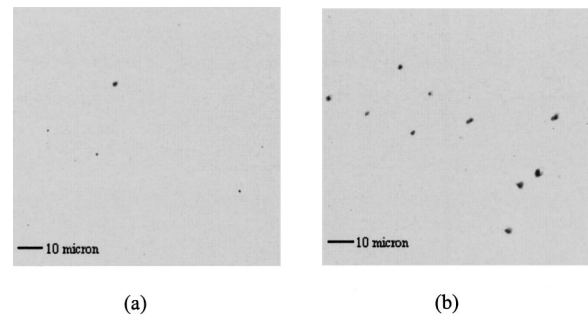


FIG. 4. Optical microscopy pictures ($\times 1000$) of the surface of GaAsN epilayers grown using: (a) the dispersive nitrogen growth mode and (b) the direct nitrogen beam growth mode.

aspect that requires more detailed investigation. Nevertheless, this observation is in reasonable agreement with the PL measurement results.

IV. CONCLUSION

This article reports the demonstration of a modified growth technique, which uses dispersive nitrogen from a rf activated plasma nitrogen source in conjunction with SSMBE for the growth of the GaAsN layers on GaAs substrate. When interrupted by a shutter, the direct nitrogen beam from the plasma source has the effect of minimizing the bombardment effect of energetic nitrogen ions on the growth surface. XRD and PL results indicate that in terms of luminescence, crystalline, and interface quality, high-quality GaAsN epilayers can be achieved using this growth mode. Preliminary comparison of light microscopy pictures suggests that the surface of the GaAsN sample grown using the dispersive nitrogen source has fewer defects compared to that of the sample grown using the direct nitrogen beam.

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