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Effects of different plasma species (atomic N, metastable N_2^*, and ions) on the optical properties of dilute nitride materials grown by plasma-assisted molecular-beam epitaxy

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This letter studies the effects of atomic N, metastable N_2^*, and ionic species on the optical properties of dilute nitride materials. $Ga_{0.8}In_{0.2}N_{0.01}As_{0.99}$ was grown using a 1% N_2 in Ar gas mix from an Applied-Epi Unibulb™ rf plasma source. Isonitrogen samples with and without ions were studied using various plasma operating conditions. Optical emission spectrometry was used to characterize relative proportions of different active nitrogen plasma species (atomic N and metastable N_2^*). Samples grown without ions and with a higher proportion of atomic N resulted in the best overall material quality, although this improvement was observed at high annealing temperatures. At lower annealing temperatures, increased blueshifts were observed for samples grown with a higher proportion of atomic N; however, there was no noticeable influence of ions on blueshift regardless of whether atomic N or metastable N_2^* was the dominant species present in the plasma. The key implication of this work is that it helps to elucidate a possible reason for some of the contradictory reports in the literature. The ions are not solely responsible for the commonly reported "plasma damage." Furthermore, we demonstrate herein that atomic N and metastable N_2^* each have different effects on the optical properties of dilute nitride materials grown by plasma-assisted molecular-beam epitaxy. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2806226]

Dilute nitride semiconductor materials[1] gained a great deal of interest during the last decade for near-infrared (IR) applications (1.2–1.6 μm) involving telecommunications[2] and solar cells.[3] However, recently, there has been a renewed interest for additional applications in the midinfrared (3–5 μm), such as countermeasures,[4] free-space communications,[5] and biological/chemical sensing.[6] Radio frequency (rf) plasma-assisted molecular-beam epitaxy (MBE) is an established growth technique for dilute nitrides and has demonstrated itself to be the preferred method for some of the applications. For example, MBE is needed for nonthermodynamically stable growths or hyperabrupt interfaces. Some of the highest performing dilute nitride lasers have been grown by plasma-assisted MBE,[7] and multijunction dilute nitride solar cells are better grown in an environment that is void of metal organic and hydride precursors used with metal-organic chemical vapor deposition (MOCVD).[8] Therefore, growth by plasma-assisted MBE continues to be a valuable growth technique for dilute nitride materials.

Unfortunately, the use of plasmas to activate nitrogen species for their subsequent incorporation into dilute nitrides has its own complications. Various active nitrogen species get generated within a plasma;[9] however, only two plasma variables most commonly get reported in the literature: (1) applied rf power and (2) gas flow rate. Reporting only these two variables causes an inherent experimental oversight when trying to study dilute nitrides grown in separate laboratories, and hence by disparate equipment. This is because the amount and proportion of different active plasma species—for a given combination of applied rf power and gas flow rate—are also dependent on other factors such as the plasma source's geometry, the power coupling mechanism, type of materials that confine the plasma, the size of the exit holes, as well as the number and orientation of these holes.[10] Therefore, growth of dilute nitrides in two separate laboratories with the identical power/flow combination will most likely lead to growth using different amounts and proportions of active plasma species.[11] This may be a main rea-

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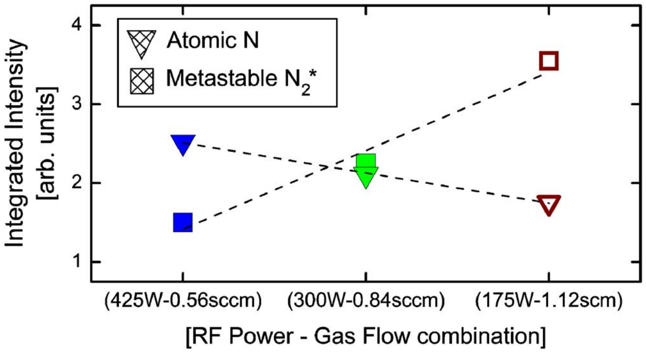

FIG. 1. (Color online) Relative integrated OES intensities that are respective to either atomic N or metastable N_2^* at each of the three isonitrogen plasma operating combinations.

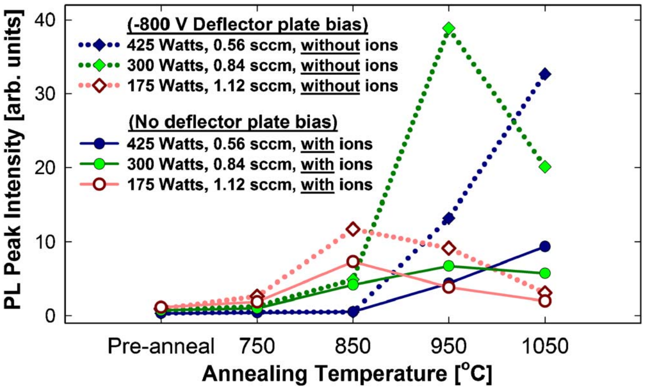

FIG. 2. (Color online) PL peak intensities upon annealing for 180 s of samples grown at three different isonitrogen conditions, each with and without ions.

son for contradicting results in the literature between various laboratories. The effects of different active nitrogen species on the optical properties of dilute nitrides has not been previously reported; therefore in this letter, we study how the optical properties are correlated to atomic N, metastable N_2^*, and ionic species.

Our samples were grown at The University of Texas at Austin in a Varian Gen-2™ MBE system equipped with an Applied-Epi Unibulb™ rf plasma source. The source was operated at three isonitrogen conditions leading to an equivalent peak emission wavelength from GaInNAs with nominal In and N compositions of 20% and 1%,[12] respectively, as determined by secondary ion mass spectrometry, which were 425 W with 0.56 SCCM (SCCM denotes cubic centimeter per minute at STP), 300 W with 0.84 SCCM, and 175 W with 1.12 SCCM. The source gas was our standard 1% N_2 in Ar mix.[13,14] dc-biased deflector plates were used to remove ions; in previous work,[15] we demonstrated that −800 V dc deflects all ions away from the substrate position. Additional details relating to our previous results and experimental apparatuses can be found elsewhere.[16]

$Ga_{0.8}In_{0.2}N_{0.01}As_{0.99}$ triple quantum wells (QWs) were grown at 520 °C. The remainder of the structure was grown at 580 °C. Additional growth details can be found elsewhere.[17] For this work, the only growth variables are the plasma conditions and/or the removal of ions during GaInNAs growth. Rapid thermal annealing (RTA) was performed in a N_2 ambient. Photoluminescence (PL) measurements were done at room temperature. The plasma's optical emission spectrometry (OES) measurements were taken using an Ocean Optics PC 1000™ spectrometer.

The OES data provide insight into relative proportions of active nitrogen species.[18,19] Ptak *et al.*[10] demonstrated that the GaN growth rate depends on fluxes from both atomic N and metastable N_2^*, thus suggesting each species can contribute to nitrogen incorporation. Recent work by Iliopoulos *et al.*[18] and Kikuchi *et al.*[19] demonstrated that OES can correlate relative concentrations of N and N_2^* to growth rates of GaN, while Carrere *et al.*[20] further demonstrated this for dilute nitrides. We therefore show in Fig. 1 the relative integrated OES intensities for each of the two active nitrogen species. The 865.8 nm OES peak of atomic N was integrated to determine its relative presence in the plasma.[14] The relative amount of metastable N_2^* was determined by integrating the broad spectrum occurring between 600–700 nm, corresponding to the energy transition from the $B\,^3\Pi_g \rightarrow A\,^3\Sigma_u^+$ electronic energy states of N_2. (This $A\,^3\Sigma_u^+$ metastable electronic state is commonly referred to as N_2^*.)[9] The broadness of the N_2^* peak in the 600–700 nm range is due to transitions from the different vibrationally excited states within each of the two electronic states.[21] The $B\,^3\Pi_g$ electronic state has a lifetime of 5–13 μs, while the $A\,^3\Sigma_u^+$ metastable electronic state has a lifetime of 1–2 s.[22] The $A\,^3\Sigma_u^+$ energy minima are located 6.2 eV above that of the N_2 molecule's minima.[9] Although there are additional active neutral species generated in a plasma, their absolute concentrations are several orders of magnitude lower than N or N_2^*, and therefore are assumed to be negligible.[23] Note in Fig. 1 that the 425 W with 0.56 SCCM combination is more favorable for the relative presence of atomic N, whereas metastable N_2^* is more favorable at the 175 W with 1.12 SCCM combination. Although the compositions of the $Ga_{0.8}In_{0.2}N_{0.01}As_{0.99}$ are nominally the same for each of the three isonitrogen combinations in Fig. 1, the dominant activated nitrogen species present in the plasma is different.

To determine the impact of the different plasma species on optical properties, Fig. 2 shows peak PL intensities measured for various samples grown under different active nitrogen species and ion conditions. Samples at each of the three isonitrogen plasma operating combinations were grown with and without ions to measure the impact of ion damage.[15] As commonly cited,[24,25] ion removal led to optical improvement in all samples. Our previously reported ion energy distributions[26] show that the conditions which favor atomic N generation (i.e., high power and low flow rates) also leads to the greatest amount and energies of the ions. Therefore, removing ions for this isonitrogen combination should lead to the greatest improvement in PL peak intensity since the most amount of ions are being removed.

However, ion damage is not the only factor influencing optical properties—otherwise ion removal should have led to comparable peak PL intensities for the different samples grown at each of the three isonitrogen combinations. Therefore, the significant result in Fig. 2 focuses on both (i) the global maximum of the PL peak intensity for each of the three isonitrogen plasma operating combinations, as well as (ii) how much RTA energy is needed to reach its respective optimal annealing condition.[27] Since the material's growth structure and atomic compositions are nominally the same for all samples in this work, this demonstrates that there is a tangible plasma-related effect on the optical properties due to atomic N versus metastable N_2^* and not just the ions alone.

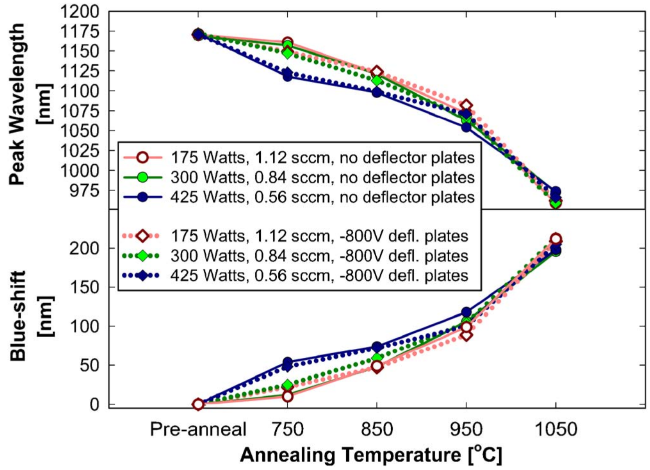

FIG. 3. (Color online) Peak PL emission wavelength and blueshift upon annealing for samples grown at different isonitrogen combinations. The use of a −800 V dc deflector plate bias removed all ions from the sample.

Figure 2 shows that samples grown under a predominance of N_2^* led to the lowest maximum PL peak intensity, which occurred at the least amount of applied RTA thermal energy (850 °C), whereas samples grown without ions and a lesser proportion of N_2^* (i.e., higher relative proportion of atomic N) led to increased PL peak intensities that reached their optimum at higher RTA thermal energies.

The effects of different plasma species on the peak PL emission wavelength can be seen in Fig. 3. We observed no significant wavelength shift specifically attributable to ions for any of the samples. This suggests that ion damage is not responsible for the commonly observed blueshift during annealing. However, there was a relatively pronounced blueshift at lower RTA temperatures for samples grown under a predominance of atomic N, both with and without ions (at 750 °C).

We are currently working to better understand this phenomenon, but we speculate that atomic N has a higher surface mobility than metastable N_2^* and is thus more likely to form the favorable Ga–N surface bonding configuration. This may happen either because atomic N has no strong dimer (N═N) to break, or because it is 3.6 eV more energetic than N_2^*,[28] and hence has more energy to hop to thermodynamically favorable lattice sites. A more favorable incorporation of atomic N can be responsible for the formation of compositional modulations of Ga—N and In—As at the edge of the QW,[25] in addition to promoting the creation of group III vacancies.[29] Upon annealing, a smoothening of these compositional modulations caused by the atomic N at QW interfaces may be leading to the more pronounced blueshift at the lower annealing temperatures shown in Fig. 3. Furthermore, if group III vacancies generated by atomic N are getting annihilated at the higher annealing temperatures, it would cause the PL peak intensity improvement observed in Fig. 2 (at temperatures >850 °C) due to removal of the nonradiative optical traps. It is still unclear to us as to the exact cause of the increased global maximum in the PL peak intensity for samples grown with a predominance of atomic N versus metastable N_2^*; however, we suspect that the N_2^* may be incorporating as the commonly observed defects involving nitrogen-nitrogen dimers on the As site $(N-N)_{As}$,[30,31] which may not be getting annealed out before the QW inevitably begins to degrade at higher annealing temperatures.[32] A comprehensive material analysis should help clarify our hypotheses and be reported upon in a future publication.

In conclusion, we studied the effects on optical properties of dilute nitrides due to different active plasma species, namely, atomic N, metastable N_2^*, and ionic species. Samples with identical atomic compositions and structures were grown but with differing proportions of active nitrogen as measured by optical emission spectrometry. We discovered that growths using predominantly N_2^* led to a lower global maximum in the PL peak intensity upon annealing than when samples were grown with a higher proportion of atomic N in the plasma. The optimal annealing temperature was also dependent on which active nitrogen species was dominant. Furthermore, removing ions did improve optical quality; although the extent of improvement was dependent on which plasma operating condition was used. Therefore, in order to fully optimize the potential of dilute nitrides for device applications, as well as providing consistency in the reporting of results from multiple laboratories, it is important to consider the effects of atomic N, metastable N_2^*, and ionic species in the plasma.

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