Enhanced nitrogen incorporation by pulsed laser annealing of GaN$_x$As$_{1-x}$ formed by N ion implantation

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We demonstrate that pulsed laser annealing followed by rapid thermal annealing greatly enhances incorporation of substitutional N in N$^+$-implanted GaAs. Films implanted to 1.8% N exhibit a fundamental band gap of 1.26 eV (a band gap reduction of 160 meV), corresponding to an N activation efficiency of 50%. The optical and crystalline quality of the synthesized film is comparable to GaN$_x$As$_{1-x}$ thin films of similar composition grown by epitaxial growth techniques. Compared to films produced by N$^+$ implantation and rapid thermal annealing only, the introduction of pulsed laser annealing improves N incorporation by a factor of 5. Moreover, we find that the synthesized films are thermally stable up to an annealing temperature of 950 °C. © 2002 American Institute of Physics. [DOI: 10.1063/1.1481196]

The anomalously strong band gap bowing in GaN$_x$As$_{1-x}$ (>150 meV for 1% of N) alloys has stimulated much interest in the properties and technological potential of this material. The many unusual electronic and optical properties of GaN$_x$As$_{1-x}$ alloys are also observed in other III–N$_x$–V$_{1-x}$ alloys such as InN$_x$P$_{1-x}$, GaN$_x$P$_{1-x}$, and Al$_x$Ga$_{1-x}$N$_x$As$_{1-x}$. Recently it was suggested that these III–N$_x$–V$_{1-x}$ alloys are members of the general class of highly mismatched alloys (HMAs) in which a small fraction of the metallic anions are replaced by more electronegative elements. The large band gap bowing in HMAs can be explained by an anticrossing interaction between localized states of the more electronegative element and the extended states of the host semiconductor matrix. Other examples of HMAs include ZnSe$_x$Te$_{1-x}$, ZnSe$_x$As$_{1-x}$, and the II–O$_x$–VI$_{1-x}$ alloys.

The formation of GaN$_x$As$_{1-x}$ thin films by N$^+$ implantation in GaAs followed by rapid thermal annealing (RTA) has been explored. Using RTA an activation efficiency of only ~10%–15% is achievable for implanted N mole fractions ($x_{\text{imp}}$) less than 0.036. The highest active N fraction reported using this technique is $x_{\text{act}}$~0.004 for $x_{\text{imp}}$~0.036.

Pulsed laser annealing (PLA) of ion implanted Si and GaAs was studied extensively in the 1970s and 1980s. It involves the melting induced by a pulsed laser of the implant-damaged or amorphized layer and its subsequent rapid epitaxial regrowth. Epitaxy is seeded at the solid–liquid interface by the crystalline bulk in a manner very similar to liquid phase epitaxy (LPE) but with the whole process occurring on a time scale between 10$^{-8}$ and 10$^{-6}$ s. Using the PLA method amorphous layers of GaAs formed by high dose implantation can be regrown into nearly perfect single crystals with electrical activities of dopants well above those achievable by furnace annealing.

In this letter we report on our efforts to increase the N incorporation in N$^+$-implanted GaAs using PLA followed by RTA.

The details of the N$^+$ implantation conditions in GaAs can be found in Ref. 18. Briefly, semi-insulating GaAs substrates were implanted with N$^+$ at multiple energies creating ~3000 Å layers of GaAs with a uniform N concentration of ~3.9 × 10$^{20}$ cm$^{-3}$. This corresponds to an $x_{\text{imp}}$~0.018. It is important to recognize that only a fraction of the implanted N will occupy As sublattice sites ($N_{\text{As}}$) after annealing and thus become “active” ($x_{\text{act}}$).

The N$^+$-implanted GaAs samples were pulsed-laser melted in air using an XeCl excimer laser ($\lambda = 308$ nm) with pulse duration ~30 ns. After passing through a multiprism homogenizer, the fluence at the sample ranged between 0.3 and 0.8 J/cm$^2$. Time resolved reflectivity (TRR) confirmed that the GaAs samples were indeed melted with melt duration of approximately 150 and 345 ns for laser fluences of 0.35 and 0.79 J/cm$^2$, respectively. Some of the samples were RTA after the PLA at temperatures between 800 and 950 °C for 10 s in flowing N$_2$.

The crystalline structure of the GaN$_x$As$_{1-x}$ samples was studied by channeling Rutherford backscattering spectrometry (c-RBS) in the (100) direction. The band gap of the films was measured using photomodulated reflectance (PR) at room temperature. Radiation from a 300 W halogen tungsten lamp dispersed by a 0.5 m monochromator was focused on the samples as a probe beam. A chopped HeCd laser beam ($\lambda = 442$ or 325 nm) provided the photomodulation. PR signals were detected by a Si photodiode using a phase-sensitive lock-in amplification system. The values of the

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The topmost spectrum was obtained from a PLA + 950 °C RTA sample using the 325 nm line of a HeCd laser. Spectra from unimplanted GaAs and N⁺-implanted GaAs subjected to RTA at 800 °C are also shown.

width of this transition narrows as the RTA temperature increases, suggesting that the quality of this Ga\textsubscript{N}\textsubscript{i},As\textsubscript{1−i} layer improves with RTA temperature.

It has been demonstrated that the band gap reduction in III–N\textsubscript{x}V\textsubscript{1−x} alloys can be explained quantitatively by an anticrossing interaction between localized N states and the extended states of the host semiconductor matrix.\textsuperscript{13−15} This interaction splits the conduction band of the alloy into two subbands. The downward shift of the lower subband (\(E_−\)) is responsible for the reduction of the fundamental band gap. Using this band anticrossing (BAC) model we calculate the active N content to be 0.9% (i.e., \(x = 0.009\) in Ga\textsubscript{N\textsubscript{i}},As\textsubscript{1−i}) for the measured band gap of 1.26 eV. From Fig. 2 the optical transitions from the valence band to the upper subband \(E_+\) is found to be approximately 1.81 eV, which is in very good agreement with the calculated value.

Another prominent feature is observed around 1.4 eV in the PR spectra of the PLA + RTA samples. This transition exhibits a slight blueshift from 1.36 to 1.4 eV as the RTA temperature increases from 800 to 950 °C. Since the N⁺-implanted GaAs region is ∼300 nm thick and the laser melted region is estimated from c-RBS to be only ∼100 nm, the underlying N-containing layer is expected to be similar to samples subjected to RTA only. Indeed, the broad line shape and the position of this transition are similar to those from a Ga\textsubscript{N\textsubscript{i}},As\textsubscript{1−i} layer formed by RTA alone. Furthermore, this transition is believed to arise from the deeper (>100 nm) N-containing layer formed via epitaxial regrowth from the melt. The line-width of this transition narrows as the RTA temperature increases, suggesting that the quality of this Ga\textsubscript{N\textsubscript{i}},As\textsubscript{1−i} layer improves with RTA temperature.

Band gap and the linewidth were determined by fitting the PR spectra to the Aspnes third-derivative functional form.\textsuperscript{22}

Figure 1 shows the c-RBS spectra from unimplanted GaAs and N⁺-implanted GaAs samples as implanted and after PLA with a pulse fluence of 0.35 J/cm\textsuperscript{2} (PLA) and subsequently RTA at 950 °C after PLA (PLA + 950 °C RTA). The (100) aligned spectrum from the as-implanted GaAs sample reveals that the sample is highly damaged yet still crystalline after N⁺ implantation. The high dechanneling and the absence of a direct scattering peak in the spectrum suggest that the majority of the damage present in the top 300 nm layer of the sample consists of extended crystalline defects.\textsuperscript{23}

The (100) aligned spectrum from the sample exposed to a pulse fluence of 0.35 J/cm\textsuperscript{2} shows a thin layer (∼100 nm) of good crystalline materials on a defective underlayer. The high dechanneling rate in the region deeper than ∼100 nm suggests that only the top 100 nm of GaAs was melted and epitaxially regrown from the liquid phase. Since the underlying GaAs was defective, a high concentration of defects is expected to accumulate at the regrowth interface. This gives rise to the high dechanneling rate between 100 and 200 nm. These interfacial defects can be removed by RTA in the temperature range of 800–950 °C. c-RBS measurements on the PLA + 950 °C RTA sample shows much improved crystalline quality.

PR measurements of the sample subjected only to PLA do not show any clear optical transition. This is consistent with the c-RBS results which indicate that the regrown layer is still defective. Distinct optical transitions are observable only in the PLA samples after RTA at temperatures higher than 800 °C. Figure 2 shows a series of PR spectra from samples processed by PLA and RTA together with an unimplanted GaAs and an N⁺-implanted GaAs sample subjected only to RTA at 800 °C. PR spectra from the laser melted and RTA (PLA + RTA) samples exhibit several well-resolved interband transitions that are distinctly different in energy from the fundamental band gap transition in the unimplanted GaAs (\(E_0\)). The main spectral feature at 1.26 eV observed in all of the PLA + RTA samples is attributed to a Ga\textsubscript{N\textsubscript{i}},As\textsubscript{1−i} layer formed via epitaxial regrowth from the melt. The line-

![C-RBS spectra](image1)

**FIG. 1.** c-RBS taken in the (100) axial direction from N⁺-implanted GaAs samples as implanted, annealed with laser pulse fluence of 0.35 J/cm\textsuperscript{2} (PLA), and with subsequent RTA at 950 °C for 10 s after PLA (PLA + 950 °C RTA).

![PR spectra](image2)

**FIG. 2.** A series of PR spectra (\(\lambda = 442\) nm modulation) from N⁺-implanted GaAs after PLA (laser fluence = 0.35 J/cm\textsuperscript{2}) and RTA at different temperatures. The topmost spectrum was obtained from a PLA + 950 °C RTA sample using the 325 nm line of a HeCd laser. Spectra from unimplanted GaAs and N⁺-implanted GaAs subjected to RTA at 800 °C are also shown.
layer that did not undergo melting. The N incorporated in this layer annealed entirely in the solid phase is estimated to be <0.1% after RTA at 950 °C.\textsuperscript{17,18}

The value of the band gap of the laser melted layers does not change significantly even at a RTA temperature of 950 °C, suggesting that the substitutional nitrogen (N\textsubscript{A}) in these layers appears to be thermally stable. We speculate that the extremely short duration of the laser melting and regrowth process inhibits the formation of nitrogen related voids, which have recently been observed in samples formed by N\textsuperscript{+} implantation followed by RTA only.\textsuperscript{24} The process of rapid melting and solidification may result in a complete local rearrangement of the atom sites leading to the formation of strong Ga–N bonds, thus stabilizing N atoms on the anion sites. The subsequent, lower temperature RTA cannot break these bonds but can improve the overall crystal quality by removing the lower energy defects. In MOCVD grown Ga\textsubscript{x}N\textsubscript{1-x} layers, N atoms on As sites are also found to be thermally stable at 950 °C.\textsuperscript{25}

Figure 3 shows a comparison of the PR spectra of two samples exposed to different laser fluences (0.35 and 0.79 J/cm\textsuperscript{2}) and RTA at 950 °C. The PR spectrum from the sample exposed to the higher fluence exhibits a much reduced intensity for the transition at \textasciitilde 1.4 eV, which is consistent with the c-RBS result showing that the entire N\textsuperscript{+} implanted layer was melted and has regrown epitaxially. However, the fundamental band gap of the layer in this sample is 1.305 eV, corresponding to \( x = \frac{1}{3} \). This lower content of substitutional N may be due to the longer duration of the melt associated with the higher fluence (345 compared to 150 ns) which would enable N atoms to migrate to the surface or coalesce to form bubbles (i.e., N-related voids).

In conclusion we have demonstrated an effective method to synthesize Ga\textsubscript{x}N\textsubscript{1-x} alloys. We have shown that thin films of Ga\textsubscript{x}N\textsubscript{1-x} with N content on the order of 1% can be synthesized by N\textsuperscript{+} implantation followed by a combination of PLA and RTA. Compared to Ga\textsubscript{x}N\textsubscript{1-x} films synthesized by N\textsuperscript{+} implantation and RTA only, the laser melting process improves the incorporation of substitutional N by a factor of 5 and enhances the thermal stability of N to a level similar to that observed for films grown by MOCVD.

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19 Both pulsed laser melting (PLM) and pulsed laser annealing (PLA) have been used in the literature to describe the same annealing phenomena process in semiconductors. We note that PLA here does not refer to an-