

# Synthesis of $\text{GaN}_x\text{As}_{1-x}$ thin films by pulsed laser melting and rapid thermal annealing of $\text{N}^+$ -implanted GaAs

K. M. Yu<sup>a)</sup> and W. Walukiewicz

*Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720*

M. A. Scarpulla and O. D. Dubon

*Materials Sciences Division, Lawrence Berkeley National Laboratory and Department of Material Science and Engineering, University of California, Berkeley, California 94720*

J. Wu, J. Jasinski, Z. Liliental-Weber, and J. W. Beeman

*Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720*

M. R. Pillai and M. J. Aziz

*Division of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts 02138*

(Received 14 March 2003; accepted 22 April 2003)

We present a systematic investigation on the formation of the highly mismatched alloy  $\text{GaN}_x\text{As}_{1-x}$  using  $\text{N}^+$ -implantation followed by a combination of pulsed laser melting and rapid thermal annealing. Thin films of  $\text{GaN}_x\text{As}_{1-x}$  with  $x$  as high as 0.016 and an activation efficiency of the implanted N up to 50% have been synthesized with structural and optical properties comparable to films grown by epitaxial deposition techniques with similar substitutional N content. The effects of  $\text{N}^+$  implantation dose, laser energy fluence, and rapid thermal annealing temperature on the N incorporation as well as optical and structural properties of the  $\text{GaN}_x\text{As}_{1-x}$  films are discussed.

© 2003 American Institute of Physics. [DOI: 10.1063/1.1582393]

## I. INTRODUCTION

Recently, we have witnessed the emergence of highly mismatched semiconductor alloys (HMAs), a class of materials whose fundamental properties are dramatically modified through the substitution of a small fraction of host atoms (less than 5 mol %) with a very different element.<sup>1,2</sup> Important examples of these highly mismatched systems include III– $\text{N}_x$ –V $_{1-x}$  alloys (e.g.,  $\text{GaN}_x\text{As}_{1-x}$ ) in which a small concentration ( $x$  up to  $\sim 0.05$ ) of the highly electronegative nitrogen atom substitutes the more metallic column V element.<sup>2–13</sup> The most striking feature of such alloys is the large N-induced bowing of the band gap, whereby the band gap decreases by as much as 180 meV per percent of N in  $\text{GaN}_x\text{As}_{1-x}$ .<sup>2,5</sup>

The large band gap bowing in HMAs can be explained by an anticrossing interaction between localized states of the more electronegative element (e.g., N compared to As in  $\text{GaN}_x\text{As}_{1-x}$ ) and the extended states of the host semiconductor matrix<sup>14,15</sup> which splits the conduction band into two subbands. In the band anticrossing (BAC) model, the dispersion relations for the upper ( $E_+$ ) and lower ( $E_-$ ) conduction subbands of  $\text{GaN}_x\text{As}_{1-x}$  are given by

$$E_{\pm}(k) = \frac{1}{2} [E_N + E_M(k) \pm \sqrt{(E_N - E_M(k))^2 + 4C_{NM}^2 x}], \quad (1)$$

where  $E_N$  is the energy of the N level,  $E_M(k)$  is the dispersion relation for the host semiconductor matrix, and  $C_{NM}$  is the matrix element describing the coupling between N states and the extended states. For  $\text{GaN}_x\text{As}_{1-x}$ , the downward

shift of the lower subband  $E_-$  can account well for the reduction of the fundamental band gap using a value of  $E_N = 1.65$  eV above the valence band maximum derived from photoluminescence measurements in N-doped GaAs<sup>16</sup> and  $C_{NM} = 2.7$  eV from fitting data on the variation of the band gap with N content.<sup>14,15</sup> The modification of the conduction band in other HMAs including  $\text{ZnS}_x\text{Se}_{1-x}$ ,  $\text{ZnS}_x\text{Te}_{1-x}$ ,  $\text{ZnSe}_x\text{Te}_{1-x}$ , and the II– $\text{O}_x$ –VI $_{1-x}$  alloys is also well described by the BAC model.<sup>1,17,18</sup>

The incorporation of these relatively small quantities of alloying species into the host semiconductor may, upon first consideration, seem as a routine challenge which can be met using today's most advanced materials synthesis techniques. However, this is far from actuality. These semiconductors are materials of extreme compositions that extend far beyond the thermodynamically allowed solubility and exist at the limit of kinetic stability. Thus, the epitaxial growth of HMAs is still a formidable task even when using the most advanced nonequilibrium deposition processes such as molecular beam epitaxy. The formation of  $\text{GaN}_x\text{As}_{1-x}$  thin films by  $\text{N}^+$  implantation in GaAs followed by rapid thermal annealing (RTA) has also been explored.<sup>19–22</sup> With RTA an activation efficiency—defined as the ratio of substitutional N in the As sublattice to implanted N—of only  $\sim 10\%$ – $15\%$  is achievable for implanted N mole fractions ( $x_{\text{imp}}$ ) less than 0.036. The highest active N fraction  $x_{\text{act}}$  reported using RTA is  $x_{\text{act}} \approx 0.004$  for  $x_{\text{imp}} \approx 0.036$ , corresponding to an activation efficiency of only 11%.<sup>21</sup>

Pulsed laser melting (PLM) of ion implanted Si and GaAs was studied extensively in the late 1970s and early 1980s.<sup>23,24</sup> It involves the melting of the implant-damaged or amorphized layer induced by the near surface absorption of

<sup>a)</sup>Electronic mail: kmyu@lbl.gov

intense (pulsed) laser radiation and the subsequent rapid epitaxial regrowth from the liquid. Epitaxy is seeded at the solid-liquid interface by the crystalline bulk in a manner very similar to liquid phase epitaxy but with the whole process occurring on a much shorter time scale, typically between  $10^{-8}$ , and  $10^{-6}$  s. It was shown that using the PLM method amorphous layers of GaAs formed by high dose implantation could be regrown into single crystals with electrical activities of dopants well above those achievable by furnace annealing.<sup>24</sup> Here we report a systematic investigation on the synthesis of  $\text{Ga}_{1-x}\text{N}_x\text{As}$  layers by  $\text{N}^+$ -implanted GaAs using pulsed laser melting followed by RTA. The effects of ion dose, laser fluences, and RTA temperature are addressed.

## II. EXPERIMENT

Nitrogen ions ( $\text{N}^+$ ) were implanted into semi-insulating GaAs wafers. Two  $\text{N}^+$  implants with energies of 80 and 33 keV with doses of  $3.5 \times 10^{15}$  and  $1.2 \times 10^{15} \text{ cm}^{-2}$ , respectively, were used to create  $\sim 2000 \text{ \AA}$ -thick layers with a uniform N atomic concentration of  $\sim 2.2 \times 10^{20} \text{ cm}^{-3}$  (1 mol. percent). Layers with total implanted N contents of 2% and 4% were also formed by increasing the total  $\text{N}^+$  dose by 2 and 4 times, respectively. All implantations were carried out using a beam current of  $\sim 0.2\text{--}0.5 \mu\text{A/cm}^2$ . We emphasize that only a fraction of the implanted N ( $x_{\text{imp}}$ ) becomes “active” by occupying the As sublattice ( $x_{\text{act}}$ ) after annealing (i.e.,  $x_{\text{act}} \leq x_{\text{imp}}$ ).

The top of the  $\text{N}^+$ -implanted GaAs samples were pulsed-laser melted in air using a XeCl excimer laser ( $\lambda = 308 \text{ nm}$ ) with pulse duration  $\sim 30 \text{ ns}$ . After passing through a multiprism homogenizer, the fluence at the sample ranged between 0.2 and  $0.7 \text{ J/cm}^2$ . The melt duration ( $\tau_{\text{melt}}$ ) was determined by monitoring the time resolved reflectivity (TRR) of the samples using an argon-ion laser. Some of the samples were subjected to rapid thermal annealing between 600 and  $950 \text{ }^\circ\text{C}$  for 10 s in flowing  $\text{N}_2$  after the PLM.

The crystalline structure of the  $\text{GaN}_x\text{As}_{1-x}$  samples was studied by channeling Rutherford backscattering spectrometry (c-RBS) in the  $\langle 100 \rangle$  direction. Selected samples were also investigated by cross-sectional transmission electron microscopy (XTEM). XTEM specimens were prepared by the standard method of mechanical thinning followed by ion milling. TEM studies were carried out using a TOPCON 002B microscope operated at 200 kV. The band gaps of the films were 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  $325 \text{ nm}$ ) provided the photomodulation. PR signals were detected by a Si or Ge photodiode using a phase-sensitive lock-in amplification system. The values of the band gap and the linewidth were determined by fitting the PR spectra to the Aspnes third-derivative functional form.<sup>25</sup>

## III. RESULTS AND DISCUSSION

### A. Nitrogen activation efficiency

In a previous report, we demonstrated that pulsed laser melting followed by rapid thermal annealing (PLM-RTA)

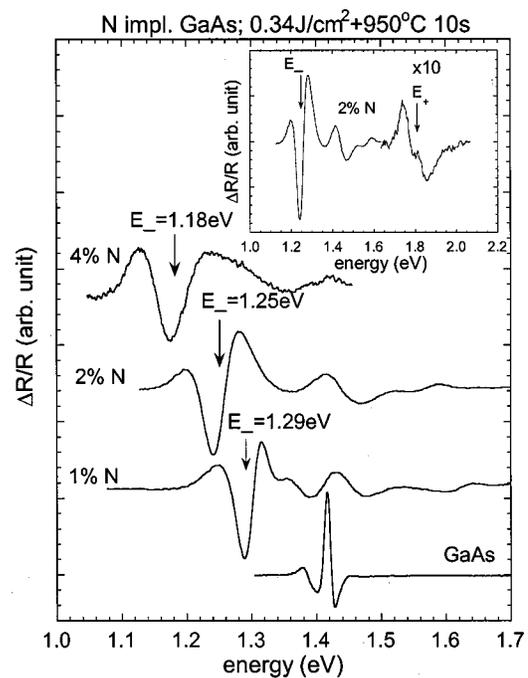


FIG. 1. PR spectra measured from a series of samples implanted with increasing levels of N ( $x_{\text{imp}}$ ) and processed by PLM at an energy fluence of  $0.34 \text{ J/cm}^2$  and subsequent RTA at  $950 \text{ }^\circ\text{C}$  for 10 s. The inset shows a PR spectrum from GaAs sample with  $x_{\text{imp}} = 2\%$  taken over a wide photon energy range (1–2.2 eV) showing both the  $E_-$  and  $E_+$  transitions.

greatly enhanced the incorporation of substitutional N in  $\text{N}^+$ -implanted GaAs.<sup>26</sup> Films implanted with 1.8% N exhibited a fundamental band gap of 1.26 eV (a band gap reduction of 160 meV), corresponding to a N activation efficiency of  $\sim 50\%$ . Compared to films produced by  $\text{N}^+$  implantation and rapid thermal annealing only, the introduction of PLM improves N incorporation by a factor of 5. It was found that subsequent RTA at temperatures higher than  $\sim 700 \text{ }^\circ\text{C}$  after PLM was essential in obtaining good quality  $\text{GaN}_x\text{As}_{1-x}$  thin films with clear optical transitions.<sup>26</sup> The optical properties and crystalline quality of these films are comparable to  $\text{GaN}_x\text{As}_{1-x}$  thin films of similar composition made by epitaxial growth techniques.

Figure 1 shows a series of PR spectra from samples implanted with increasing amounts of N processed by PLM with energy fluence of  $0.34 \text{ J/cm}^2$  and subsequently RTA at  $950 \text{ }^\circ\text{C}$  for 10 s. Such PLM-RTA postimplantation treatments represent the “optimum” conditions giving rise to clear, sharp optical transitions. The effects of different PLM and RTA conditions will be discussed later. PR spectra from all of the PLM-RTA samples shown in Fig. 1 exhibit distinct optical transitions across the fundamental band gap of the material. The optical transition energies of the various samples are indicated in the figure. A monotonic decrease in the band gap with increasing implanted N content  $x_{\text{imp}}$  is clearly observed in Fig. 1, indicating an increasing fraction of N is incorporated in the As sublattice with increasing  $x_{\text{imp}}$ .

The band gaps—transitions from the valance band maximum to the lower subband  $E_-$ —of the  $\text{GaN}_x\text{As}_{1-x}$  layers synthesized by  $\text{N}^+$  implantation and subsequent optimum

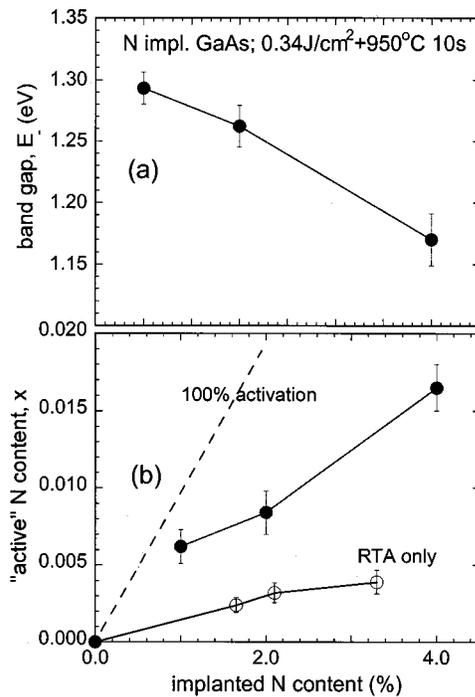


FIG. 2. (a) Band gap energies determined from the PR spectra shown in Fig. 1. (b) Active N content estimated using the band anticrossing model and the values of  $E_-$  determined from the PR spectra in (a). The dashed line in (b) represents 100% activation for the implanted N. Also shown in (b) is the active N content in  $\text{GaN}_x\text{As}_{1-x}$  layers synthesized by  $\text{N}^+$  implantation followed by RTA (800 °C for 10 s) alone.

PLM-RTA are plotted in Fig. 2(a) as a function of implanted N. The amount of N incorporated in the As sublattice (active N) for these  $\text{GaN}_x\text{As}_{1-x}$  layers can be calculated using the BAC model for HMAAs expressed in Eq. (1). Figure 2(b) shows the active N contents calculated using the values of  $E_-$  from Fig. 2(a) and Eq. (1). The dashed line represents 100% activation, i.e.,  $x_{\text{act}} = x_{\text{imp}}$ . Also shown is the active N content in  $\text{GaN}_x\text{As}_{1-x}$  layers synthesized by  $\text{N}^+$  implantation followed by RTA (800 °C 10 s) alone from Ref. 21.

The results in Fig. 2(b) demonstrate that using the PLM-RTA method, the N incorporation efficiency is  $\sim 50\%$  (slightly lower for the high dose case), over five times higher than that observed in samples synthesized by RTA alone. This can be attributed to the extremely short melt duration ( $\sim 200$  ns) and regrowth process that promotes N substitution in the As sublattice and inhibits the formation of nitrogen related voids, which have recently been observed in samples formed by  $\text{N}^+$  implantation followed by RTA only.<sup>27</sup>

In addition to the  $E_-$  level, the BAC model also predicts an upper subband  $E_+$  as a result of the anticrossing interaction of the localized N states and the extended conduction band states of GaAs. This electronic transition to the  $E_+$  level has been observed in  $\text{GaN}_x\text{As}_{1-x}$  thin films grown by epitaxial techniques for  $x > 0.008$  when it becomes resolvable from the spin-orbit transition ( $E_0 + \Delta$ ).<sup>13,14</sup> The inset of Fig. 1 shows a PR spectrum taken over a wide photon energy range (1–2.2 eV) from the 2%  $\text{N}^+$ -implanted GaAs followed by optimum PLM-RTA processing where  $x \approx 0.009$ . In addition to the fundamental band gap transition at 1.25 eV, a transition at 1.8 eV is observed. This high energy transition

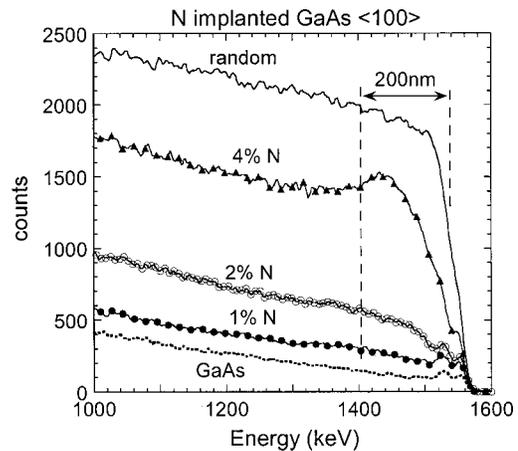


FIG. 3. c-RBS spectra from  $\text{N}^+$ -implanted GaAs samples with  $x_{\text{imp}} = 1\%$ , 2% and 4% taken in the  $\langle 100 \rangle$  axial direction. The  $\langle 100 \rangle$  aligned and random spectra from an unimplanted GaAs sample are also shown.

is in excellent agreement with transition to the  $E_+$  level as calculated using Eq. (1) (1.81 eV). The observation of the  $E_+$  transition further confirms the successful formation of  $\text{GaN}_x\text{As}_{1-x}$  thin films by  $\text{N}^+$ -implantation in GaAs processed by PLM-RTA.

## B. Crystalline structure of $\text{N}^+$ -implanted GaAs layers processed by PLM and RTA

The structural damage of GaAs by  $\text{N}^+$  implantation was studied by channeling RBS in the  $\langle 100 \rangle$  orientation. Figure 3 shows the c-RBS spectra from unimplanted GaAs and  $\text{N}^+$ -implanted GaAs samples with  $x_{\text{imp}} = 1\%$ , 2% and 4%. Notice that the  $\langle 100 \rangle$  aligned spectra from the  $\text{N}^+$ -implanted GaAs sample do not reach the "random" (nonchanneling) level. This suggests that the sample is highly damaged yet still crystalline even for the sample with  $x_{\text{imp}} = 4\%$ . This is consistent with the high dynamic annealing rate of GaAs at room temperature during implantation.<sup>28</sup> For the samples with  $x_{\text{imp}} = 1\%$  and 2%, dechanneling (change in slope in the c-RBS spectrum) is observed in the spectra with no observable direct scattering peak, indicating that the majority of the damage present in the top 200 nm layer of the sample consists of extended crystalline defects.<sup>29</sup> For the sample with  $x_{\text{imp}} = 4\%$ , a direct scattering peak is observed at  $\sim 150$  nm below the surface. This can be attributed to the presence of either displaced Ga and As atoms or amorphous regions in the sample.

The c-RBS spectra from a  $\text{N}^+$ -implanted GaAs sample with  $x_{\text{imp}} = 2\%$  for the as-implanted condition, after PLM with  $0.34 \text{ J/cm}^2$ , and after PLM followed by RTA at 950 °C for 10 s are shown in Fig. 4(a). The  $\langle 100 \rangle$  aligned spectrum from the sample exposed to a pulse fluence of  $0.34 \text{ J/cm}^2$  alone shows complete recrystallization of the implanted layer. The normalized yield  $\chi$  (the ratio of channelled to random yields) in this recrystallized layer is  $\sim 0.08$ , slightly higher than that for perfect unimplanted GaAs ( $\chi = 0.04$ ). This suggests that the epitaxially regrown layer is still defective after PLM, likely containing extended crystalline defects.

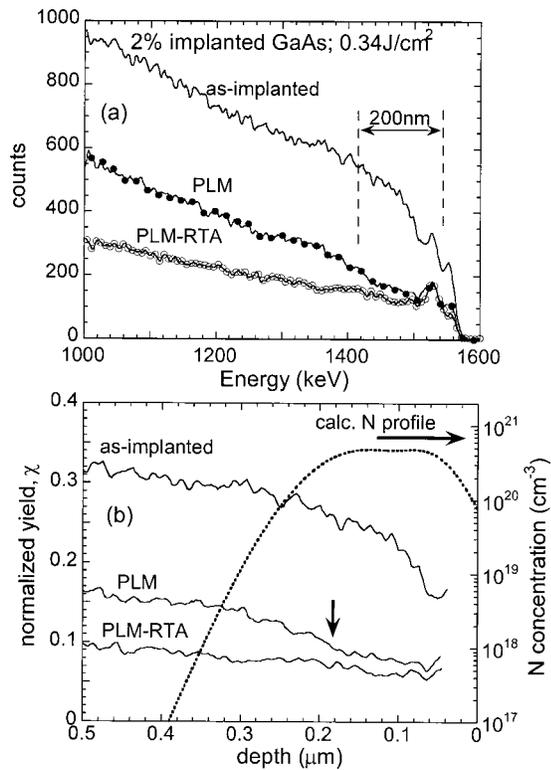


FIG. 4. (a) c-RBS spectra from  $\text{N}^+$ -implanted GaAs samples with  $x_{\text{imp}}=2\%$  in the as-implanted condition, after PLM at an energy fluence of  $0.34 \text{ J/cm}^2$ , and after PLM followed by RTA at  $950^\circ\text{C}$  for 10 s. (b) The normalized yields (ratio of the channelled to random yields) of the c-RBS data from (a) are plotted against depth below the GaAs surface. The calculated N distribution is also shown in the figure.

Figure 4(b) shows the normalized RBS yields from Fig. 4(a) plotted against depth below the GaAs surface. In addition the calculated N distribution<sup>30</sup> for the 2%  $\text{N}^+$  implantation is also included. For the sample made by PLM alone, a high dechanneling slope is noticeable at  $\sim 0.18 \mu\text{m}$  below the surface (indicated by the arrow), suggesting that the region above this point melted and epitaxially regrew from the liquid phase at this energy fluence. Since the underlying GaAs was still defective due to the end-of-range implantation damage, a high concentration of defects accumulates at the regrowth interface. Additional RTA at  $950^\circ\text{C}$  for 10 s removed these interfacial defects. c-RBS measurements on the PLM-RTA sample shows much improved crystalline quality, approaching that for unimplanted GaAs. The RBS results are consistent with the optical experiments that show clear optical transitions only after RTA following PLM.

The structure of the 2%  $\text{N}^+$ -implanted sample subjected to PLM-RTA was further studied by XTEM. Figure 5 shows bright-field XTEM images comparing the microstructure of a sample with  $x_{\text{imp}}=2\%$  processed only by RTA with a sample treated by the PLM-RTA process (with energy fluence of  $0.34 \text{ J/cm}^2$ ). The RTA-only sample [Fig. 5(a)] shows a highly defective layer at depths of about  $0.1\text{--}0.4 \mu\text{m}$ . In this region numerous dislocations loops are present. Many of these loops, especially the large ones, interact and form networks. A high density of nanometer-sized bubbles, which are probably filled with nitrogen gas, is also seen in this region.<sup>27</sup>

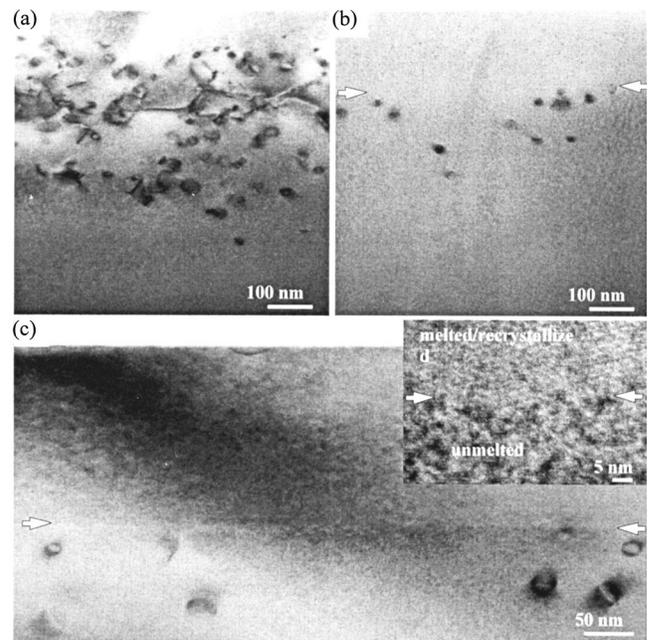


FIG. 5. Bright-field symmetrical cross-sectional TEM images of  $\text{N}^+$ -implanted GaAs samples with  $x_{\text{imp}}=2\%$  for the following process conditions: (a) RTA at  $950^\circ\text{C}$  for 10 s only and (b) PLM at an energy fluence of  $0.34 \text{ J/cm}^2$  followed by RTA at  $950^\circ\text{C}$  for 10 s. (c) Bright-field two-beam cross-sectional TEM image of the sample shown in (b). The inset of (c) shows a high-resolution image of the interface region. Note the much higher disorder/clustering in the area below the interface.

This highly defective area is then followed by a region containing the “end-off range” defects that extends to a depth of  $\sim 0.5 \mu\text{m}$ . These are mostly extrinsic dislocations loops located on  $\{111\}$  planes.

In contrast to the RTA-only sample the XTEM image of the PLM-RTA sample [Fig. 5(b)] shows that the subsurface layer is free from structural defects. Close examination of Fig. 5(b) reveals a sharp interface at  $\sim 0.2 \mu\text{m}$  below the surface separating two regions indicated by arrows in the figure. We believe this to be the interface between the laser-melted and then recrystallized top layer and the unmelted substrate. This interface is clearly visible in the bright-field image taken under two beam conditions shown in Fig. 5(c). High-resolution images of this interfacial region shown in the inset of Fig. 5(c) show that there is much less crystalline disorder/clustering in the area above than in the area below this interface. However, small bubble-like defects typically less than 5 nm in size are still present. We note that the ‘end-off range’ defects remain below this interface. XTEM images on samples PLM with  $0.61 \text{ J/cm}^2$  reveals that the laser melted region extended to  $>0.3 \mu\text{m}$ .

### C. Effects of laser energy fluence on N activation

Figure 6 shows the normalized yield versus depth obtained from c-RBS spectra measured from a series of 2%  $\text{N}^+$ -implanted GaAs samples after PLM. The threshold energy fluence for melting GaAs was determined by TRR to be  $\sim 0.2 \text{ J/cm}^2$ . From the onset of the high dechanneling slope in the c-RBS spectra, we estimate the melt-regrown layers for samples subjected to  $0.24$  and  $0.34 \text{ J/cm}^2$  laser

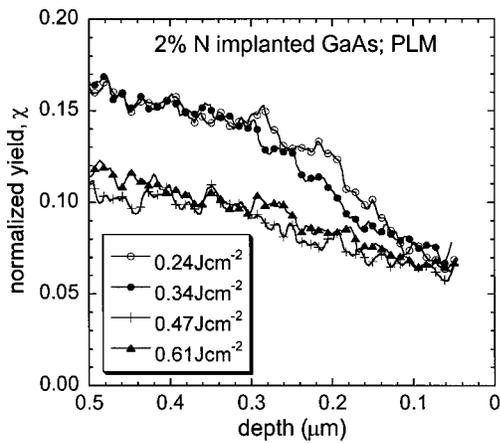


FIG. 6. Normalized yield as a function of depth obtained from c-RBS spectra from a series of N<sup>+</sup>-implanted GaAs samples with  $x_{\text{imp}}=2\%$  after PLM at an energy fluence in the range of 0.24–0.61 J/cm<sup>2</sup>.

pulses to be  $\sim 0.12$  and  $0.18 \mu\text{m}$ , respectively. For energy fluences  $>0.47 \text{ J/cm}^2$ , the dechanneling slope in the c-RBS spectra is no longer observable, indicating that the laser-melted layer exceeds the regions with significant amounts of implant damage ( $>0.25 \mu\text{m}$ ). These ion channeling results are in good agreement with the XTEM measurements mentioned previously.

PR spectra from the samples shown in Fig. 6 with additional RTA at 950 °C for 10 s are shown in Fig. 7. The fundamental band gap transition at 1.25 eV is not affected by the laser energy fluence. This suggests that increasing the energy fluence does not influence the N incorporation in the film. Similar results on the lack of energy fluence dependence on N incorporation are also observed for the sample with  $x_{\text{imp}}=1\%$  N. Since the melt depth exceeds the implanted GaAs layer thickness for the high laser energy fluence, one might expect a decrease in the N incorporation if the N atoms are free to redistribute in the melted layer to form N<sub>2</sub> molecules.

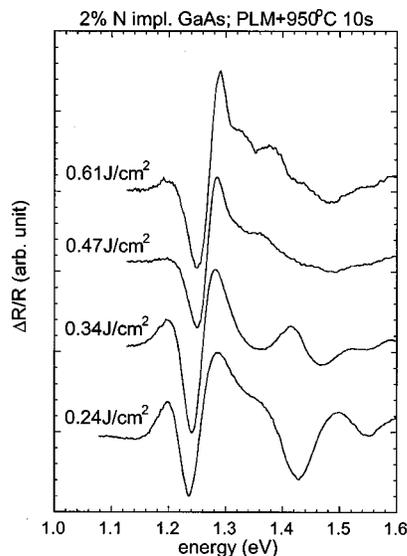


FIG. 7. PR spectra from the samples shown in Fig. 5 with additional RTA at 950 °C for 10 s.

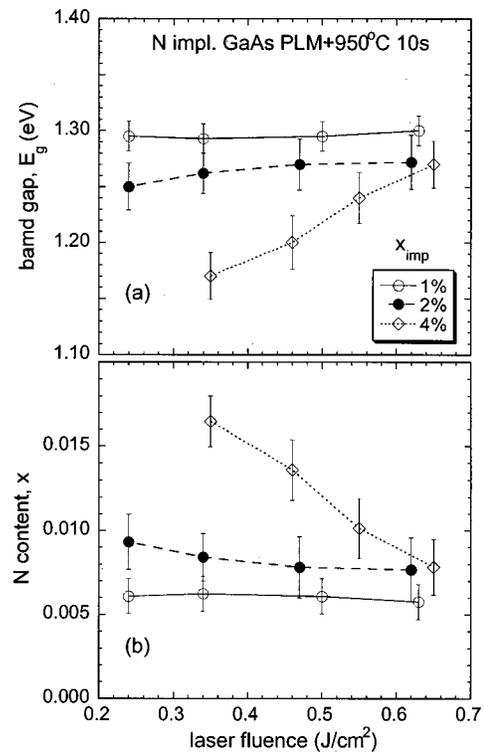


FIG. 8. Band gap energy and active N concentration ( $x_{\text{act}}$ ) determined from PR spectra as a function of PLM energy fluence. The samples were annealed at 950 °C for 10 s following the PLM process.

The fact that the incorporation of N atoms does not depend on energy fluence suggests that they do not diffuse significantly in the short melt duration of hundreds of nanoseconds.

In the PR spectrum from the sample exposed to an energy fluence of 0.24 J/cm<sup>2</sup>, another prominent feature is observed at around 1.4 eV. Since the N<sup>+</sup>-implanted GaAs region is  $\sim 0.2 \mu\text{m}$  thick and the laser-melted region is estimated from c-RBS to be only  $\sim 0.1 \mu\text{m}$  for this energy fluence, 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 GaN<sub>x</sub>As<sub>1-x</sub> layer formed by RTA alone.<sup>21</sup> In addition to the increase in melting depth as measured by c-RBS and TEM, raising the energy fluence also results in an increase in the melt duration  $\tau_{\text{melt}}$ , which was measured to be  $\sim 100$ – $300 \text{ ns}$  for the energy fluence range of 0.24–0.61 J/cm<sup>2</sup>.

The effect of laser energy fluence on the band gap (as determined from PR spectra) and on N incorporation in GaAs samples with  $x_{\text{imp}}=1\%$ ,  $2\%$ , and  $4\%$  is displayed in Figs. 8(a) and 8(b), respectively. While the band gap and thus the N incorporation is not dependent on the energy fluence for the samples with  $x_{\text{imp}}=1\%$  and  $2\%$ , the band gap of the samples with  $x_{\text{imp}}=4\%$  followed by PLM and RTA depends strongly on the energy fluence of the laser pulse. Increasing the energy fluence in this case results in an increase in the band gap and a decrease in the amount of incorporated N. At a fluence of 0.61 J/cm<sup>2</sup>, a similar amount of incorporated N ( $\sim 0.8\%$ ) is found for both the 2% and 4% N-implanted samples. This can be attributed to the high N

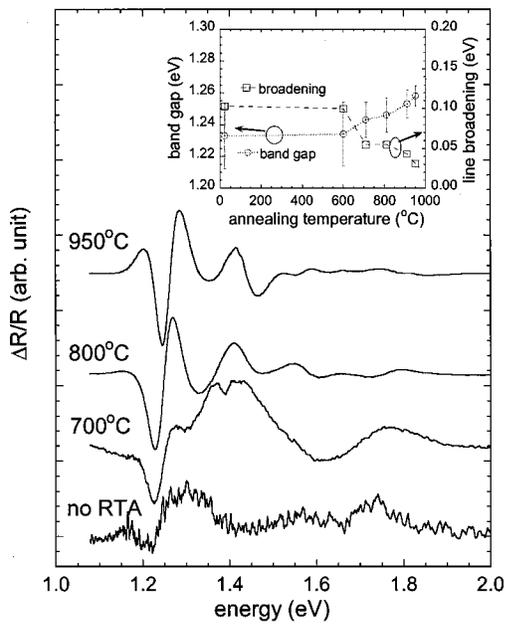


FIG. 9. A series of representative PR spectra from  $N^+$ -implanted GaAs samples with  $x_{\text{imp}}=2\%$  after PLM at an energy fluence of  $0.34 \text{ J/cm}^2$  followed by RTA for 10 s in the temperature range of 600–950 °C. The band gaps measured by PR and the linewidth of the optical transitions are plotted as a function of the RTA temperature (inset).

content in the GaAs that exceeds the kinetic limit of solubility even for the short melt duration of  $\sim 300 \text{ ns}$ . Hence, the longer duration of the melt associated with the higher fluence enables the N atoms to migrate to the surface or to coalesce and form bubbles (i.e., N-related voids). This may account for the reduced N activation in these high  $x_{\text{imp}}$  samples as the energy fluence increases.

#### D. Effects of RTA temperature

As mentioned earlier, distinct optical transitions in  $N^+$ -implanted GaAs are observable only after PLM and RTA at temperatures higher than 700 °C. This is consistent with the c-RBS measurements on the PLM samples that showed the presence of structural defects after the PLM process. Figure 9 shows a series of representative PR spectra from  $N^+$ -implanted GaAs samples with  $x_{\text{imp}}=2\%$  after PLM at a fluence of  $0.34 \text{ J/cm}^2$  followed by RTA for 10 s in the temperature range of 600–950 °C. Only a very weak and vague optical transition is observed for the sample processed only by PLM due to the high concentration of defects that remains in the regrown layer. The optical transition attributable to the band gap at  $\sim 1.2\text{--}1.3 \text{ eV}$  becomes very clear after RTA at 700 °C. The linewidth of this transition continues to narrow as the RTA temperature increases, indicating the improvement in the crystallinity of the layer.

The inset of Fig. 9 shows the band gap and the linewidth of the optical transitions measured by PR as a function of the RTA temperature. A slight, gradual increase in the band gap with increasing RTA temperature is observed. For RTA at 950 °C, the band gap increases by 20 meV with respect to the sample not treated by RTA. This change in the band gap, although observable, accounts to only  $\sim 12\%$  of the total

band gap reduction and corresponds to a reduction in active N incorporated in the layer from  $x_{\text{act}}=0.0107$  to 0.0093.

As a comparison, for  $N^+$ -implanted GaAs samples subjected to RTA only, annealing above 870 °C resulted in less than 0.1% N incorporation in GaAs.<sup>21</sup> We believe that this is due to the presence of a high concentration of vacancies in the N-implanted samples. Upon RTA these vacancies recombine and also act as sinks for the N atoms, promoting the clustering of N into voids. A recent transmission electron microscopy investigation revealed that in the  $N^+$ -implanted GaAs sample after RTA at 950 °C a very high density of N-related small voids, with an average size of about 2–3 nm is present in the implanted layer.<sup>27</sup> In the case of PLM the process of rapid melting and solidification may result in the annihilation of implantation-induced vacancies as well as 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 short range atomic diffusion and rearrangement. In metalorganic chemical vapor deposition grown  $\text{GaN}_x\text{As}_{1-x}$  layers, N atoms on As sites are also found to be thermally stable at RTA at 950 °C.

A narrowing of the linewidth of optical transitions observed in PR measurement occurs as the RTA temperature is increased. This is depicted in the inset of Fig. 9. Increasing the RTA temperature results in the more effective removal of structural imperfections present after PLM processing. The improved crystal quality of the implanted layer leads to sharper optical transitions. For samples synthesized by PLM and RTA at 950 °C, the linewidth of the optical transition becomes comparable to that from  $\text{GaN}_x\text{As}_{1-x}$  thin films with similar N composition that were epitaxially grown by metalorganic chemical vapor deposition ( $< 30 \text{ meV}$ ).<sup>13</sup>

#### IV. CONCLUSION

In conclusion we have carried out a systematic investigation on the formation of the highly mismatched alloy  $\text{GaN}_x\text{As}_{1-x}$  using  $N^+$  implantation followed by a combination of pulsed laser melting and rapid thermal annealing. With an optimized treatments on a GaAs substrate implanted with 4%  $N^+$ ,  $\text{GaN}_x\text{As}_{1-x}$  thin films with  $x$  as high as 0.016 have been synthesized. For implanted N concentrations below 4%, a N activation efficiency as high as 50% can be achieved. Increasing the energy fluence of the pulsed laser above the threshold ( $\sim 0.2 \text{ J/cm}^2$ ) increases both the melt duration and melt depth. We found that energy fluence does not alter the N incorporation for concentrations of implanted N below 2%. For samples implanted with 4% N, increasing the PLM energy fluence dramatically reduces the N incorporation to a value close to that observed for samples implanted with N to a level of 2%. As the RTA temperature is increased, a gradual decrease in the linewidth of the PR transition and a slight increase in the band gap are noticed. This indicates that the RTA process following PLM improve the crystallinity of the layers with little N deactivation.

## ACKNOWLEDGMENTS

This work is supported by the Director, Office of Science, Office of Basic Energy Science, Division of Materials Sciences and Engineering, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. M.A.S. acknowledges support from an NSF graduate research fellowship. The work at Harvard was supported by NASA Grant No. NAG8-1680.

- <sup>1</sup>W. Walukiewicz *et al.*, Phys. Rev. Lett. **85**, 1552 (2000).
- <sup>2</sup>See for example, Semiconductor Science and Technology Vol. 17, 2002, Special Issue: III–N–V Semiconductor Alloys.
- <sup>3</sup>S. Sakai, Y. Ueta, and Y. Terauchi, Jpn. J. Appl. Phys., Part 1 **32**, 4413 (1993).
- <sup>4</sup>M. Kondow, K. Uomi, K. Hosomi, and T. Mozume, Jpn. J. Appl. Phys., Part 2 **33**, L1056 (1994).
- <sup>5</sup>K. Uesugi, N. Morooka, and I. Suemune, Appl. Phys. Lett. **74**, 1254 (1999).
- <sup>6</sup>J. F. Geisz, D. J. Friedman, J. M. Olson, S. R. Kurtz, and B. M. Keyes, J. Cryst. Growth **195**, 401 (1998).
- <sup>7</sup>M. Kondow, T. Kitatani, M. C. Larson, K. Nakahara, K. Uomi, and H. Inoue, J. Cryst. Growth **188**, 255 (1998).
- <sup>8</sup>D. J. Friedman, J. F. Geisz, S. R. Kurtz, D. Myers, and J. M. Olson, J. Cryst. Growth **195**, 409 (1998).
- <sup>9</sup>S. R. Kurtz, A. A. Allerman, E. D. Jones, J. M. Gee, J. J. Banas, and B. E. Hammons, Appl. Phys. Lett. **74**, 729 (1999).
- <sup>10</sup>J. N. Baillargeon, K. Y. Cheng, G. E. Hofler, P. J. Pearah, and K. C. Hsieh, Appl. Phys. Lett. **60**, 2540 (1992).
- <sup>11</sup>W. Shan, W. Walukiewicz, K. M. Yu, J. Wu, J. W. Ager, E. E. Haller, H. P. Xin, and C. W. Tu, Appl. Phys. Lett. **76**, 3251 (2000).
- <sup>12</sup>W. G. Bi and C. W. Tu, J. Appl. Phys. **80**, 1934 (1996).
- <sup>13</sup>W. Shan *et al.*, Phys. Rev. B **62**, 4211 (2000).
- <sup>14</sup>W. Shan, W. Walukiewicz, J. W. Ager III, E. E. Haller, J. F. Geisz, D. J. Friedman, J. M. Olson, and S. R. Kurtz, Phys. Rev. Lett. **82**, 1221 (1999).
- <sup>15</sup>J. Wu, W. Shan, and W. Walukiewicz, Semicond. Sci. Technol. **17**, 860 (2002).
- <sup>16</sup>D. J. Wolford, J. A. Bradley, K. Fry, and J. Thompson, in *Proceedings of the 17th International Conference on the Physics of Semiconductors*, edited by J. D. Chadi and W. A. Harrison (Springer, New York, 1984), p. 627.
- <sup>17</sup>K. M. Yu *et al.*, Appl. Phys. Lett. **80**, 1571 (2002).
- <sup>18</sup>K. M. Yu, J. Wu, W. Walukiewicz, J. W. Beeman, J. W. Ager, E. E. Haller, I. Miotkowski, and A. Ramdas, J. Electron. Mater. **31**, 754 (2002).
- <sup>19</sup>W. Shan, K. M. Yu, W. Walukiewicz, J. W. Ager, E. E. Haller, and M. C. Ridgway, Appl. Phys. Lett. **75**, 1410 (1999).
- <sup>20</sup>K. M. Yu, W. Walukiewicz, W. Shan, J. Wu, J. Beeman, J. W. Ager III, E. E. Haller, and M. C. Ridgway, Mater. Res. Soc. Symp. Proc. **647**, O13.3.1/R8.3.1 (2001).
- <sup>21</sup>K. M. Yu *et al.*, J. Appl. Phys. **90**, 2227 (2001).
- <sup>22</sup>K. M. Yu, Semicond. Sci. Technol. **17**, 785 (2002).
- <sup>23</sup>*Laser and Electron Beam Processing of Materials*, edited by C. W. White and P. S. Peercy (Academic, New York, 1980).
- <sup>24</sup>J. S. Williams, in *Laser Annealing of Semiconductors*, edited by J. M. Poate and J. W. Mayer (Academic, New York, 1982), p. 385.
- <sup>25</sup>D. E. Aspnes, Surf. Sci. **37**, 418 (1973).
- <sup>26</sup>K. M. Yu, W. Walukiewicz, J. W. Beeman, M. A. Scarpulla, O. Dubon, M. R. Pillai, and M. Aziz, Appl. Phys. Lett. **80**, 3958 (2002).
- <sup>27</sup>J. Jasinski, K. M. Yu, W. Walukiewicz, Z. Liliental-Weber, and J. Washburn, Appl. Phys. Lett. **79**, 931 (2001).
- <sup>28</sup>R. A. Brown and J. S. Williams, J. Appl. Phys. **81**, 7681 (1997).
- <sup>29</sup>L. C. Feldman, J. W. Mayer, and S. T. Picraux, *Materials Analysis by Ion Channeling* (Academic, New York, 1982).
- <sup>30</sup>PROFILE, Ion Beam Profile Code version 3.20, Implant Sciences Corp. 107 Audubon Rd., #5, Wakefield, MA 01880.