Origin of improved luminescence efficiency after annealing of Ga(In)NAs materials grown by molecular-beam epitaxy

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Positron-annihilation measurements and nuclear reaction analysis [utilizing the $^{14}N(d,p)^{15}N$ and $^{14}N(d,He)^{12}C$ reactions] in conjunction with Rutherford backscattering spectrometry in the channeling geometry were used to study the defects in as-grown Ga(In)NAs materials grown by molecular beam epitaxy using a radio-frequency plasma nitrogen source. Our data unambiguously show the existence of vacancy-type defects, which we attribute to Ga vacancies, and nitrogen interstitials in the as-grown nitride–arsenide epilayers. These point defects, we believe, are responsible for the low luminescence efficiency of as-grown Ga(In)NAs materials and the enhanced diffusion process during annealing. © *2001 American Institute of Physics.*
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Group III-nitride arsenides are very promising materials for 1.3 and 1.55 μm telecommunication optoelectronic devices grown on GaAs substrates.[1–4] It is well known that the incorporation of nitrogen into GaAs causes the bulk band gap to decrease dramatically, but it also deteriorates the crystalline quality of Ga(In)NAs materials.[1,2,5] Many studies have shown that annealing significantly improves the luminescence efficiency of these alloys [the photoluminescence (PL) intensity typically increases by a factor of 20], which has been attributed to a significant reduction in the concentration of competing nonradiative defects,[1,2,6] but it also results in a blueshift of the emission. The blueshift has been attributed to nitrogen outdiffusion and group III interdiffusion.[2,6,8] The identity of the nonradiative defects, however, remains unclear. The defects present in as-grown Ga(In)NAs epilayers were believed to be related to the N ions-induced damage, and an electrical or magnetic field was applied to remove the residual energetic ions.[7,8] It was also postulated that the nonradiative traps were due to hydrogen impurities since hydrogen concentration in the samples changed when annealing.[9,10] However, for nitride–arsenides grown by solid-source molecular beam epitaxy (MBE) using a rf-plasma cell (with no hydrogen present) the same increase of luminescence efficiency with annealing was observed.[6] Recently, it was reported that interstitial nitrogen could be responsible for the low luminescence efficiency of unannealed Ga(In)NAs materials with higher nitrogen content.[5,6]

Positron annihilation spectroscopy can be used to study point defects in semiconductors, and in particular, vacancies. Positrons trapped at vacancy defects are experimentally observed as an increase in the positron lifetime and a narrowing of the momentum distribution of the annihilating electron-positron pairs.[11]

On the other hand, Rutherford backscattering spectrometry (RBS) using a high energy ion beam is a well established method to quantify the composition of matrix elements and impurities in near-surface layers of many semiconductor materials, including GaAs.[12] When the ion beam is aligned parallel to a low index crystallographic direction in a single crystal sample, the backscattering yield can decrease by as much as two orders of magnitude due to channeling. This phenomenon can be used to probe defect structures and lattice site locations in crystalline materials. Since RBS methods are not sensitive to nitrogen atoms, nuclear reaction analysis (NRA) was employed in this study utilizing the $^{14}N(d,p)^{15}N$ and $^{14}N(d,He)^{12}C$ reactions.

In this work, we use both positron-annihilation measurements and NRA in conjunction with RBS to study the point defects present in as-grown Ga(In)NAs materials grown by MBE using a rf-plasma cell. Our data reveal a high density of nitrogen interstitials and Ga vacancies. These defects, we believe, are responsible for the low luminescence efficiency of as-grown Ga(In)NAs materials and the enhanced diffusion process during annealing.

The samples for this study were grown using a gas-source MBE system. Group III fluxes are produced by thermal effusion cells, group V flux is provided by a thermally cracking AsH_3, and reactive nitrogen is provided by a rf-plasma cell. The Ga(In)NAs films were grown around 450 °C to incorporate N into the Ga(In)As epilayers on GaAs. The detailed growth conditions were described elsewhere.[2,5] After growth, *ex situ* rapid thermal annealing was applied by using halogen lamps and flowing N_2 gas ambient.

The N-implanted sample was used for the calibration of secondary ion mass spectroscopy (SIMS) measurements of

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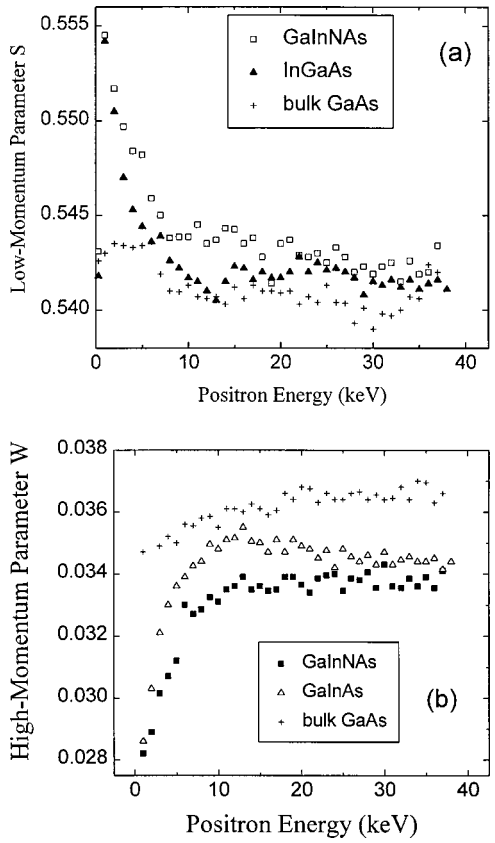

FIG. 1. (a) Low-momentum parameters S and (b) high-momentum parameter W as a function of positron incident energy in as-grown $Ga_{0.94}In_{0.06}N_{0.02}As_{0.98}$ sample. For comparison, the data for a bulk GaAs (defect free) and a $Ga_{0.99}In_{0.01}As$ sample grown under the same condition are also shown.

nitrogen concentration in Ga(In)NAs epilayers. SIMS measurements were provided by VG Ionex IX70S instrument. Cs^+ ions were used as primary ions and the primary ion energy used was 12 keV. The nitrogen concentration was deduced from the SIMS profile based on the signal ratio of $^{83}GaN/^{69}Ga$.[5]

Positron annihilation spectra were measured using a positron beam with the variable energy $E=0-40$ keV. The 511-keV-annihilation line was measured using a Ge detector with an energy resolution of 1.3 at 511 keV. The shape of the line was described in terms of low and high electron-momentum parameters S and W, which were determined using conventional energy windows.[13] The S parameter represents the fraction of positrons annihilating mainly with the valence electrons with a longitudinal momentum component of $p_L < 3.7\times10^{-3}\ m_0c$, where m_0 is the electron mass and c the speed of light. The W parameter is the fraction of annihilations with the core electrons with a large momentum component of $11\times10^{-3}\ m_0c < p_L < 29\times10^{-3}\ m_0c$.

The S and W parameters in 1 μm-thick as-grown $Ga_{0.94}In_{0.06}N_{0.02}As_{0.98}$ epilayer on GaAs were measured at 300 K as a function of the position beam energy E shown in Fig. 1. For comparison, a reference $Ga_{0.99}In_{0.01}As$/GaAs sample grown under the same growth conditions is also shown in the figure. It is well known that positrons get trapped at neutral and negative vacancy defects with a typical binding energy of >1 eV, and the electron momentum distribution at vacancies is narrower than in the bulk.[13] Therefore, the increase of S and the decrease of W parameters are thus clear signs of vacancy defects in the samples. The value of S is above the reference level S_B and W is below W_B found in all as-grown Ga(In)NAs samples, thus indicating that the samples contain vacancy-type defects. Since the annihilation parameter S and W fall on the line between the GaAs lattice and Ga vacancy, we conclude only Ga vacancies act as positron traps.[14] The concentration C_V of Ga vacancy (or complex) can thus be calculated using S parameter data in the equation

$$C_V = \frac{N_{at}}{\mu_V \tau_B}\frac{S-S_B}{S_V-S},$$

where N_{at} is the atomic density and $\tau_B = 230$ ps is the positron lifetime in the GaAs lattice. At 300 K we use the positron trapping coefficient $\mu_V(300\,\mathrm{K}) = 1.4\times10^{15}\,\mathrm{s}^{-1}$, and for the Ga vacancy we use $S_{V(\mathrm{Ga})} = 1.015\ S_B$.[14]

The concentration of Ga vacancy was calculated to be $(4.2\pm0.2)\times10^{16}\,\mathrm{cm}^{-3}$ in the GaInNAs sample and $(1.5\pm0.1)\times10^{16}\,\mathrm{cm}^{-3}$ for the reference GaInAs (N-free) epilayer, respectively. This result suggests that the Ga vacancy-type defects present in the N containing samples partly related to the energetic N ion-induced damage, since there is inevitably a low current of ions reaching the substrate (the rf plasma cell will produce a much lower current of ions than dc source). The other source is due to the lower growth temperature used for the nitride–arsenide materials to avoid the phase separation. As a result, the insufficient migration of the cations will contribute to the formation of Ga vacancies.

The S and W parameters in annealed (750 °C 30 s) GaInNAs samples were also measured, and their values are almost the same as the reference levels S_B and W_B, indicating most of the Ga vacancies present in the as-grown samples are annealed out after RTA treatment.

For the channeling measurements, a beam of 1.3 MeV deuterium ions with a current of 40 nA was used. The first spectrum taken was always the on-axis alignment, and the acquisition time for the critically aligned spectrum was kept below the time at which irradiation damage could have accumulated to an amount affecting the minimum yield of the sample. In order to determine the concentration of interstitials in the epilayer, a channel in a low index direction [100] was probed. By comparing the N yields from spectra obtained in random and channeling direction, the amount of nitrogen in the [100] channel could be calculated. This concentration of interstitial nitrogen represents a lower limit for the total concentration, since some of the possible interstitial sites were shadowed by lattice atoms and would only be accessible through different channels.

Figure 2 shows the nuclear reaction yield as a function of energy obtained from the 100-nm-thick as-grown and annealed GaN_xAs_{1-x} epilayer (with a 10-nm-thick GaAs cap layer) with the ion beam aligned with the [100] (surface normal). The intensity of the random nitrogen is proportional to the total nitrogen concentration. Higher energies correspond to smaller depth below the sample surface. The total nitrogen concentration in this sample, as measured by SIMS, was $(6.7\pm0.6)\times10^{20}\,\mathrm{cm}^{-3}$ ($x=3.02\%$). Assuming that the N interstitials are within the $\langle100\rangle$ channel, measurements of the NRA yield in the channeling and random directions unam-

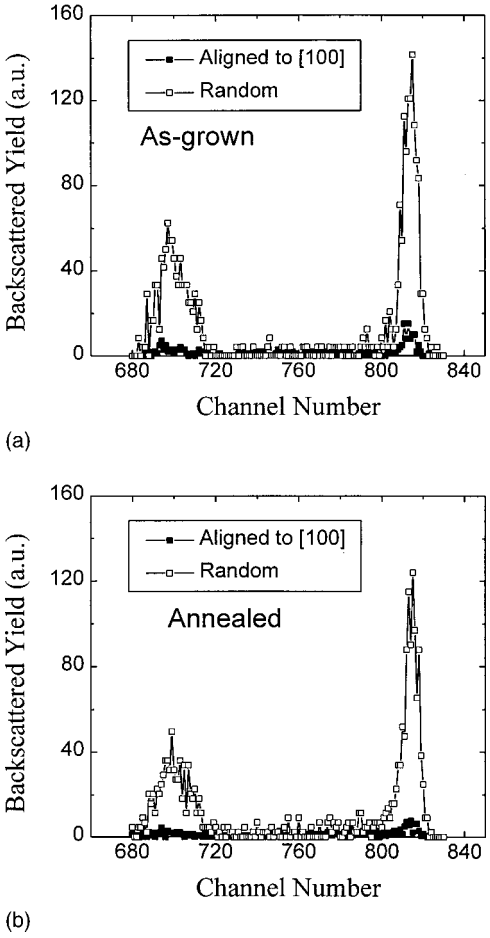

FIG. 2. Nuclear reaction yields as a function of energy (shown as channel number) obtained for a random direction and aligned to [100] from: (a) as-grown and (b) annealed $GaN_{0.03}As_{0.97}$ epilayer grown by GSMBE.

biguously show that $(2.5\pm0.2)\%$ of the nitrogen is in an interstitial lattice site for the as-grown sample (the mechanisms for interstitial N formation and related configurations are discussed in Ref. 5). After anneal at 750 °C for 30 s the fraction of N interstitial decreases to $(0.30\pm0.04)\%$, and a slightly increase of the interstitial to substitutional ratio of RBS yields from GaAs is observed, indicating most of the N interstitials reoccupying the substitutional sites possibly through a kickout mechanism in which an interstitial nitrogen kicks out arsenic from the lattice resulting in an interstitial arsenic and an substitutional nitrogen atom.[15] In addition, we find even for the low N content as-grown sample ($x=0.72\%$) the concentration of N interstitial is very high $[(2.3\pm0.2)\times10^{19}\,\mathrm{cm}^{-3}]$, indicating N interstitial is the major defect formed in nitride–arsenides due to the large size mismatch between the As and the N atom.[5]

The existence of high density of N interstitials and Ga vacancies in the as-grown nitride–arsenide materials will significantly affect device performance, since they would introduce band-gap levels affecting the carrier capture and recombination as well as transport process. Therefore, the nitride–arsenide materials must be annealed to obtain device quality material. Unfortunately, the annealing out of these defects also leads to an enhanced inter-diffusion (As–N interdiffusion through kickout mechanism and/or vacancy-assistant group III interdiffusion in the case of GaInNAs/GaAs) which accounts for the fast blueshift of the emission wavelength at the initial stages of the anneal.[2,8] An alternative is to improve the design of the rf-plasma source reducing the ion-induced damage or incorporate more indium atoms in the epilayer inhibiting the N interstitial formation. The role of indium is twofold: (1) the indium also causes the bulk band gap to decrease, thus less N atoms are required in the nitride–arsenides for certain wavelength applications; (2) a highly compressive strain in the epilayer induced by the indium incorporation makes N atoms energetically prefer to occupy the As sublattice than the interstitial sites during the growth.

In conclusion, we use both positron-annihilation measurements and NRA in conjunction with RBS to study the defects in as-grown Ga(In)NAs materials grown by molecular beam epitaxy using a rf-plasma source. Our data reveal a high density of nitrogen interstitials $[(2.3\pm0.2)\times10^{19}\,\mathrm{cm}^{-3}]$ and Ga vacancies $[(4.2\pm0.2)\times10^{16}\,\mathrm{cm}^{-3}]$. We believe these point defects are responsible for the low luminescence efficiency of as-grown Ga(In)NAs materials, which would help to understand the growth and annealing process of Ga(In)NAs materials and other physical properties.

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