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ABSTRACT

We have examined the influence of electron irradiation and rapid thermal annealing on photoluminescence emission from GaAsNBi alloys. Electron irradiation of a 1-eV compressively strained GaNAsBi-on-GaAs epilayer, grown by molecular beam epitaxy and subsequently rapidly thermally annealed, is found to induce much stronger photoluminescence than what is observed for an identical as-grown sample upon annealing. At the same time, annealing of the irradiated sample caused a negligible spectral blueshift and reduced alloy potential energy fluctuations. These irradiation-related phenomena occurred without a change in the alloy macroscopic composition as revealed by x-ray diffraction and are mainly related to the nitrogen incorporated into non-substitutional sites in the quaternary alloy.

Given the strong and complementary nature of the impact of N and Bi incorporation on the GaAs band structure, co-alloying to form the quaternary dilute nitride-bismide alloy $GaAs_{1-x-y}N_xBi_y$ provides significant opportunities for band structure engineering.[1–3] N (Bi) incorporation primarily impacts the conduction band (valence band) structure and introduces tensile (compressive) in-plain lattice strain with respect to a GaAs substrate, suggesting that the bandgap, valence band structure, band offsets, and strain can all be readily engineered.[4–6] Initial experimental studies have revealed the expected giant reduction and bowing of the alloy bandgap, confirming that $GaAs_{1-x-y}N_xBi_y$ alloys offer an interesting platform from the perspective of photonic and photovoltaic device development.[7]

However, the incorporation of both nitrogen and bismuth into the III–V lattice requires low-temperature growth conditions, even lower than those required to incorporate only nitrogen, thus causing formation of the defects, which may act as non-radiative centers, as previously experienced in all the members of the highly mismatched alloys.[1,3] The density of defects can be reduced by annealing. However, annealing induces an undesired blueshift of the alloy bandgap, especially at elevated temperatures (>600 °C) where the effect of annealing on the alloy photoluminescence (PL) intensity is pronounced.[8] In quaternary GaInNAs alloys, the annealing-induced blueshift of the alloy bandgap is thought to be a point defect-assisted phenomenon.[9]

Electron irradiation of semiconductors is a straightforward way of generating point defects or altering the existing ones.[10,11] Applying electron irradiation to GaAsNBi alloys allows a useful insight into the role of defects in annealing-induced modification of their luminescence performance. Moreover, such a study would be useful for many applications because similar defects are introduced during the processing of GaAsNBi-based devices as well as during device operation in a radiation environment (e.g., space solar cells) so that information on the irradiation stability of the dilute nitride bismides could also be extracted from such experiments.

For these studies, 100-nm thick ternary and quaternary alloys, namely, $GaAs_{0.992}N_{0.008}$, $GaAs_{0.966}Bi_{0.034}$, and $GaAs_{0.959}N_{0.007}Bi_{0.034}$, were grown on semi-insulating (001) GaAs substrates by molecular-beam epitaxy (MBE) using solid Ga, As_4, and Bi sources and a radio frequency nitrogen plasma source. The layers were grown at $345 \pm 15\,^{\circ}C$, with an As_4/Ga beam equivalent pressure ratio of ≈20 and a growth rate of 1 μm/h. The mole fractions of N and Bi were determined using channeling ion beam analysis, as described elsewhere.[3] Following growth, ∼2 mm × 2 mm pieces of each sample were irradiated with 6 MeV electrons up to the fluence of 10^{15} electrons/cm^2. For both as-grown and electron-irradiated ternary and quaternary alloys, rapid thermal annealing (RTA) was performed for 1 min at 650 °C under a dry nitrogen atmosphere using a GaAs proximity cap, which we term "as-grown" and "e^-- irradiated" GaAsN, GaAsBi, and GaAsNBi. For all samples, high resolution x-ray diffraction (XRD) was performed using a Rigaku Smart Lab diffractometer. As shown in Fig. 1, XRD spectra for the GaAsN, GaAsBi, and GaAsNBi layers reveal similar positions and line-widths of the epilayer peaks, independent of e^- irradiation and/or RTA, indicating minimal changes in N and Bi mole fractions and overall crystalline quality.

For photoluminescence (PL) spectroscopy, the samples were mounted inside a closed-cycle He cryostat and photoexcited with the second harmonic (532 nm) line of a YAG:Nd CW laser operating at 100 mW. The luminescence was collected in the front surface configuration into a monochromator and detected by a thermoelectrically cooled InGaAs photodetector (Hamamatsu).

As seen in Fig. 2, the PL intensity of the e-irradiated GaAsNBi sample is less than half than that of the corresponding as-grown sample, revealing a large introduction of non-radiative defects by the

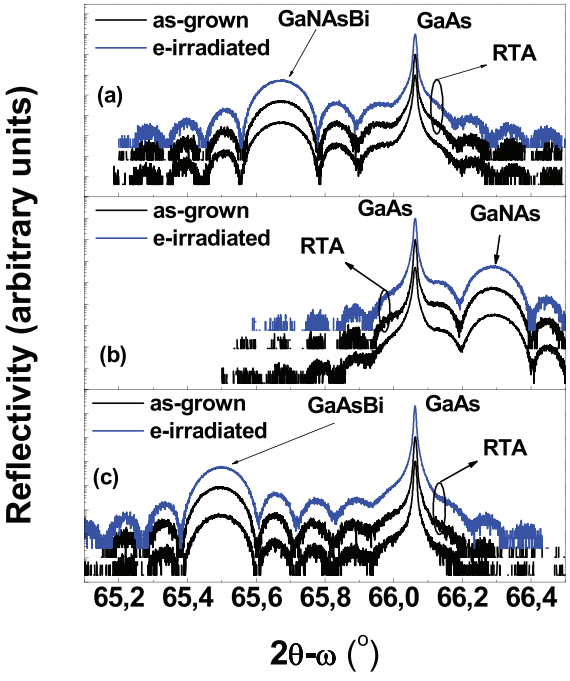

FIG. 1. X-ray diffraction (XRD) curves from the as-grown and e-irradiated (a) $GaAs_{0.959}N_{0.007}Bi_{0.034}$/GaAs, (b) $GaAs_{0.992}N_{0.008}$/GaAs, and (c) $GaAs_{0.966}Bi_{0.034}$/GaAs samples recorded before and after rapid thermal annealing (RTA).

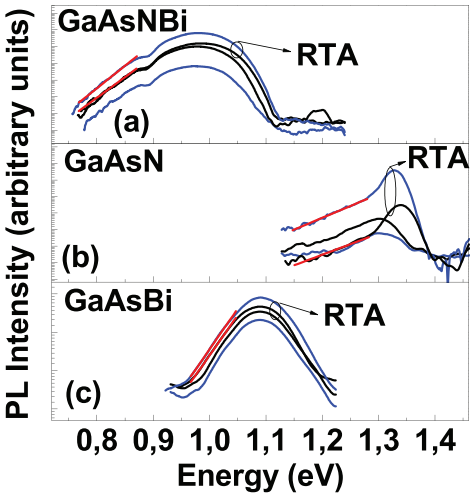

FIG. 2. 7-K PL recorded before and after RTA from the as-grown (continuous dark lines) and e-irradiated (continuous blue lines): (a) $GaAs_{0.959}N_{0.007}Bi_{0.034}$/GaAs, (b) $GaAs_{0.992}N_{0.008}$/GaAs, and (c) $GaAs_{0.966}Bi_{0.034}$/GaAs samples. Linear fits (red lines) to the low-energy side of the PL transitions.

electron irradiation. The PL of the e-irradiated ternary GaAsN alloy is even more affected, becoming upon irradiation one third than that of the corresponding as-grown sample, whereas the PL of the e-irradiated dilute bismide alloy, GaAsBi, only reduced with 17%. This shows a better radiation hardness of the GaAsBi alloys compared to the N-containing ones, grown at the same low temperature. It is clear that the incorporation of N into GaAs(Bi) makes the resulting matrix much more sensitive to electron irradiation as compared to the GaAs matrix containing only Bi. That is to say, the noticeable deterioration seen in PL from the GaAsNBi sample upon electron irradiation is mainly linked to the presence of N in the quaternary alloy, though the presence of Bi cannot be completely ruled out.

Despite the initial PL deterioration produced, one can observe that the electron irradiation appears to induce a remarkable enhancement in PL intensity with annealing in the N-containing ternary GaAsN and quaternary GaAsNBi alloys and only a minor PL enhancement in the N-free ternary GaAsBi alloy. Notably, the PL intensity of the annealed e-irradiated GaAsN and GaAsNBi became more than six and two times more intense, respectively, than that of their corresponding annealed non-irradiated samples, indicating that the electron irradiation promotes a more efficient removal of the non-radiative defects in these materials upon thermal annealing. In contrast, the PL intensity of the e-irradiated GaAsBi material became with 27% only larger than that of the non-irradiated material upon annealing. These indicate that the presence of N in GaAsNBi is mainly linked to the remarkable effect of the electron irradiation on curing the alloy non-radiative defects on annealing. The small efficiency improvement that occurred in the irradiated GaAsBi suggests that other N-free mechanisms are also at work, however, to a less extent. It is worth mentioning that an enhancement in PL promoted by electron irradiation was previously seen in both strained and lattice-matched quaternary GaInNAs/GaAs alloys upon annealing,[10,11] suggesting that electron irradiation followed by thermal treatment could be a useful technique for healing the poor optical quality of other quaternary members of the dilute nitride family such as GaAsNSb or GaAsNP alloys.

One can further remark that the observed irradiation-promoted enhancement in PL intensity in the GaAsNBi sample occurred with a negligible 1.5 meV (2 nm) spectral blueshift of the PL peak, whereas a larger PL blueshift of 8 meV (10 nm) was seen for the as-grown sample upon the RTA. This further indicates that the irradiation with electrons not only improves the luminescence efficiency on annealing but also attenuates the mechanism responsible for the annealing-induced blueshift in GaAsNBi alloys. This is different from what was previously observed in the case of GaInNAs alloys in both highly strained high-In GaInNAs/GaAs quantum wells[10] and low-In GaInNAs nearly lattice matched to GaAs,[11] where an additional annealing-induced PL blueshift always accompanied the irradiation-promoted PL enhancement seen in this alloy upon annealing. The annealing-induced blueshift of PL also reduced from 38 meV (28 nm) to 26 meV (19 nm) for the non-irradiated and irradiated GaAsN samples, respectively, indicating, as in the case of GaAsNBi material, a noticeable irradiation-promoted attenuation (with 12 meV) of the mechanism responsible for the spectral PL blueshift on annealing in GaNAs alloys. In other words, the PL from the e-irradiated + RTA GaAsN sample is with 12 meV (9 nm) red shifted compared to the corresponding as-grown + RTA GaAsN sample. In contrast, no spectral shift (within the experimental errors $\leq$1 meV) was encountered upon the RTA neither for the as-grown nor for the irradiated GaAsBi samples, suggesting that the mechanism of the annealing-induced blueshift in these alloys is not activated at 650 °C. The above results on irradiated ternaries indicate that not only the irradiation-promoted enhancement in PL but also the decrease in the PL spectral blueshift on annealing seen in the GaAsNBi material are mainly connected with the incorporation of nitrogen into the quaternary alloy.

Figures 3(a)–3(c) show the variation of the peak intensities I(T) of the PL with the inverse of absolute temperature 1/T from the as-grown and e-irradiated GaAsNBi and GaAsN samples upon annealing. The I(T) values can be very well described by the following expression:

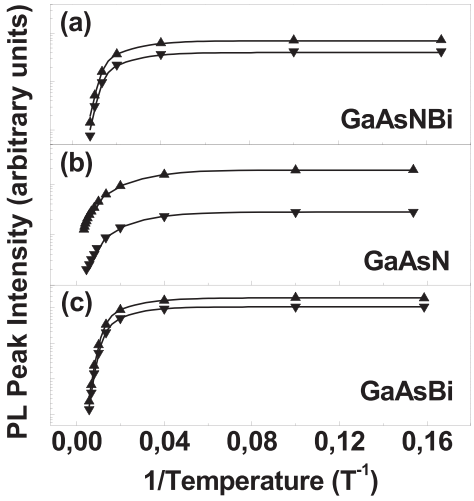

FIG. 3. Arrhenius plots of intensity of PL from the as-grown (down-pointing triangles) and e-irradiated (up-pointing triangles) (a) $GaAs_{0.959}N_{0.007}Bi_{0.034}/GaAs$, (b) $GaAs_{0.992}N_{0.008}/GaAs$, and (c) $GaAs_{0.966}Bi_{0.034}/GaAs$ after the RTA treatment. The solid curves are the best fits of Eq. (1) to the experimental points, yielding the activation energies E_1 and E_2 and prefactors c_1 and c_2 given in Table I.

$$I(T) = I(0)/[1 + c_1 \exp(-E_1/k_BT) + c_2 \exp(-E_2/k_BT)], \quad (1)$$

which can be interpreted in terms of two thermally activated loss processes with the activation energies E_1 and E_2, with the prefactors c_1 and c_2 measuring the efficiency of the corresponding loss mechanisms 1 and 2, respectively.[10] We ascribe the observed two loss processes to thermally activated transfers of carriers to non-radiative recombination centers, in this image, the prefactors c_i, $i = 1, 2$, being related to the density of the non-radiative centers i. In Table I, we give E_1, E_2, c_1, and c_2 as the best fist to the experimental I(T). E_1 and E_2 are not much affected by annealing as well as irradiation and annealing for both samples, indicating that the same processes take place in both the non- and e-irradiated GaAsNBi, GaAsN, and GaAsBi samples. The low-T prefactor c_1 is also somewhat less influenced by annealing with or without the prior irradiation step, showing that the low-temperature loss process is not affected. Instead, the high-T prefactor c_2 is clearly smaller for the annealed e-irradiated GaAsNBi and GaNAs samples as compared to the only annealed ones, indicating a reduction of the high-temperature loss mechanism of PL, beneficial for use of the alloys in devices operating at higher temperatures. This is supported by the observation of the room-temperature PL only in the RTA-treated e-irradiated GaAsN sample and also only in the annealed e-irradiated GaAsNBi sample when the laser power was increased by an order of magnitude. This makes the irradiated and thermally treated GaAsNBi alloy suitable for use in optical devices operating at high concentration carrier levels.

Also taking the XRD results into account, it is clear that the annealing-induced PL blueshift in both the as-grown and e-irradiated GaAsN and GaAsNBi layers is not explainable in terms of variations in the macroscopic alloy composition. In other words, the PL blueshift due to the RTA at 650 °C must originate from a microscopic mechanism occurring inside the (irradiated) ternary and quaternary alloys, which leave their initial concentrations of substitutional N and Bi atoms unchanged. It was previously proposed[1] that the elimination (reduction) of the bandgap energy tail, caused by potential fluctuations due to microscopic alloy inhomogeneities, could be the cause for the annealing-induced PL blueshift in GaAsNBi alloys.

The low-energy (long-wavelength) side of the low-temperature PL spectra of the GaAsNBi and GaAsN samples is well described by an exponential function, as expected for a density of states (DOS) tail caused by a fluctuating potential. Fitting an exponential function I(E) and $\exp(E/E_0)$, where I(E) gives the strength of emission at photon energy E, to the low-energy tail of semilogarithmic PL emission at low

TABLE I. Activation energies and prefactors obtained by the best fit of Eq. (1) to the experimental photoluminescence intensities as a function of inverse temperature.

Annealed sample	E_1 (meV)	c_1	E_2 (meV)	c_2
GaNAs	6.6 ± 0.2	4.5 ± 0.4	28.6 ± 1.9	44.5 ± 5.8
e-Irradiated GaNAs	6.5 ± 0.3	4.7 ± 0.3	28.9 ± 1.4	26.9 ± 2.4
GaNAsBi	8.1 ± 0.4	5.5 ± 0.6	48.2 ± 3.8	3113 ± 161
e-Irradiated GaAsNBi	7.8 ± 0.3	5.3 ± 0.5	47.3 ± 3.2	2585 ± 123
GaAsBi	8.5 ± 0.4	2.7 ± 0.3	42.4 ± 1.4	229 ± 29
e-Irradiated GaAsBi	7.1 ± 0.6	2.0 ± 0.3	39.5 ± 2.1	191 ± 36

temperature, one obtains an estimate for the characteristic energy E_0 of the localized states, from $1/E_0 = d[\ln I(E)]/dE$, where the term on the right-hand side gives the slope of a line fitted to the experimental points, as shown in Figs. 2(a)–2(c). The derived E_0 amounts to 41.3 and 58.8 meV for the annealed e-irradiated GaAsNBi and GaAsN samples, respectively, whereas larger values (smaller slopes) of 50.4 and 72.3 meV were obtained for the annealed references GaAsNBi and GaAsN samples, respectively. In other words, less potential fluctuations are encountered in the irradiated N-containing samples compared to the corresponding non-irradiated ones after annealing. In contrast, 46.6 and 47.5 meV were derived for the annealed e-irradiated and as-grown GaAsBi samples, respectively, indicating that the electron irradiation has only a minor effect on the potential fluctuations of GaAsBi upon annealing. The lesser potential fluctuations, which translate into a smaller DOS tail of the bandgap energy, observed upon annealing in the e-irradiated GaAsNBi and GaAsN samples compared to their non-irradiated references are expected to rather lead to an enlargement and not to a clear reduction of the annealing-induced PL blueshift in the e-irradiated N-containing layers. This rules out the previously proposed reduction of the bandgap energy tail as the main cause for the PL blueshift on annealing in our GaNAs(Bi) alloys and suggests searching for other mechanisms.

It is known that a large amount of the impinging plasma-activated nitrogen atoms and/or molecules incorporates into off-substitutional sites in GaAs, generating point defects, for instance, N–N and N–As interstitial pairs being among the most favorable ones from the energy formation point of view.[12,13] This scenario is also expected to occur when growing GaAsNBi by MBE, taking into account that GaAsNBi is grown even at lower temperatures than normally used to synthetize GaAsN[14] and, moreover, the presence of Bi itself appears to support the off-site incorporation of N.[2] These N-related defects could act as non-radiative and/or scattering centers for carriers, explaining the drastic decrease in luminescence efficiency and broadening of the emission linewidth with the increasing N content. At the same time, these N-related interstitial defects could noticeably influence the alloy optical bandgap (for instance, the N–N and N–As interstitial pairs were theoretically found to redshift and blueshift, respectively, the GaAsN alloy bandgap),[12,13] their removal and/or structural transformation upon annealing leading to a spectral PL shift without a noticeable change in the alloy composition. Thus, the magnitude of the PL blueshift at annealing temperatures $<700\,^{\circ}C$, at which the diffusion of substitutional nitrogen is negligible, would be mainly dictated by the changes the thermal treatment makes in the amount and/or structure of different native N-related defects coexisting at the same time in the alloy and, hence, in the influence these defects have on the alloy bandgap. Previous ion beam analysis data for GaAsN taken before and after RTA showed a dissociation of the N–N pairs into substitutional N plus N–As pairs.[15] This scenario, which is likely to take place in GaAsNBi alloys, could be influenced by electron irradiation, for example, by enhancing on annealing the N substitutionals at the expense of the N interstitials under the form of N–As pairs, thus generating a decrease in the PL blueshift.

In summary, irradiation with 6 MeV electrons to the fluence of 10^{15} electrons/cm^2 was found to deteriorate the low-temperature photoluminescence of the 100 nm $GaN_{0.007}As_{0.959}Bi_{0.034}$ thin film grown on GaAs by molecular beam epitaxy at 350 °C. When rapid thermally annealed at 650 °C for 1 min, a remarkable enhancement in PL intensity resulted, which was much larger than the enhancement in intensity seen in the corresponding as-grown sample annealed under the same conditions. At the same time, the annealing-induced PL blueshift and potential energy fluctuations reduced. The observed irradiation-induced changes in PL upon thermal treatment occurred without a change in the alloy macroscopic composition and were found to be mainly related to the presence of the N off-site incorporated into the quaternary alloy.

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DATA AVAILABILITY

The data that support the findings of this study are mainly available within the article and from the corresponding author upon reasonable request.

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