

Temperature dependencies of annealing behaviors of GaInNAsSb/GaNAs quantum wells for long wavelength dilute-nitride lasers

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The photoluminescence (PL) spectra of GaInNAs(Sb)/GaNAs quantum well samples emitting around 1.5 μm , annealed at different temperatures and for different durations, were compared. Two distinct processes with widely different temperature dependencies are identified: PL intensity improvement at the beginning of annealing and PL intensity degradation when overannealed. The degradation process has a much steeper temperature dependence than the improvement process, so lower-temperature, longer-duration annealings result in both a higher photoluminescence intensity and a broader process window than higher-temperature, shorter-duration annealings. The lowest threshold of 1.55 GaInNAs(Sb) lasers up to now was obtained exclusively with short, hot annealings, this finding offers another method of further improving dilute-nitride laser performance. Similar trends are found for different compositions and thicknesses of GaInNAs(Sb). © 2007 American Institute of Physics. [DOI: 10.1063/1.2746944]

Dilute-nitride materials have been actively researched for their potential to enable low-cost high-density GaAs-based optoelectronic devices for optical communications and interconnects in the 1.2–1.6 μm wavelength range.^{1–3} The high-quality growth of these materials, however, has proven quite challenging due to plasma-induced damage and the low solubility of nitrogen in the GaAs matrix. Significant improvements and optimization in growth methods and material quality have been made, enabling low thresholds of 1.3 and 1.55 μm edge-emitting lasers.^{4–6} Annealing has been incorporated as a standard process for dilute nitrides to remove as-grown defects and improve materials quality.

There have been many reports of the annealing properties of dilute nitrides,^{7–10} but most of the studies limited either the temperature or duration to one value or a very small set of values,^{11–14} or discussed only Sb-free GaNAs or GaInNAs.¹⁵ Some early annealing studies may not have revealed the intrinsic annealing properties of GaInNAs(Sb) due to the suboptimal growth conditions used in early dilute-nitride research. Therefore, a more extensive and systematic annealing study on high-quality dilute-nitride samples is necessary to reveal the real properties of GaInNAs(Sb) under annealing. The 1.55 μm GaInNAsSb quantum well (QW) samples studied in this report are nominally the same as the QWs used in the best 1.55 μm GaInNAsSb lasers that we recently reported.^{16,17}

For most practical optoelectronic devices, QW growth is followed by growth of relatively thick upper structures, such as the upper cladding in edge-emitting lasers or the top distributed Bragg reflector in vertical cavity surface emitting lasers. During the upper layer growth, the QW is subjected to hours of *in situ* annealing at a temperature higher than the optimal QW growth temperature. It has been suggested that

this may result in overannealing of the QWs, degrading the laser performance.⁶ Therefore, annealing studies of dilute nitrides must be conducted with consideration of this inevitable *in situ* annealing.¹⁸

Samples were grown by solid-source molecular beam epitaxy on semi-insulating (100) GaAs. Indium and gallium were supplied with thermal evaporation cells, and dimeric arsenic and monomeric antimony were supplied with cracking cells. Reactive nitrogen was supplied by a rf plasma cell operated with 0.5 SCCM (SCCM denotes cubic centimeter per minute at STP) of ultrapure nitrogen gas and 300 W at 13.56 MHz. Ionized species were removed from the molecular beam by deflection plates at the exit aperture of the plasma cell, biased to –40 and 0 V.³ The active region was nominally a single 70 Å GaInNAsSb QW surrounded on either side by 200 Å GaNAs barriers grown at 440 °C. The active region was grown upon a 3000 Å GaAs buffer and capped with 500 Å of GaAs grown at 580 °C. Growth temperature was monitored by both band edge absorption and pyrometry. Grown samples were then annealed in a rapid thermal annealing (RTA) chamber, with a GaAs cap wafer on top of the sample to minimize arsenic desorption. Nitrogen was used as the ambient gas in the RTA chamber. For the annealing temperature, the thermocouple temperature is reported instead of the real temperature due to difficulty of directly measuring the sample temperature.

The samples were first annealed at different temperatures of 720–820 °C, for a fixed duration of 1 min. The measured peak photoluminescence (PL) intensity is shown in Fig. 1. As previously reported by many researchers, the PL intensity initially increases with temperature as defects are annealed, but starts to degrade when the temperature gets too high. The optimum occurs around 760 °C. We have been annealing our GaInNAs(Sb) samples using this fixed 1 min duration with great results. But other annealing methods, such as longer or shorter durations than 1 min, have not been explored.

To explore other possibilities of annealing, we first annealed samples at 700 °C for 10–150 min, as shown in Fig. 2. The result resembles that in Fig. 1, in that the PL

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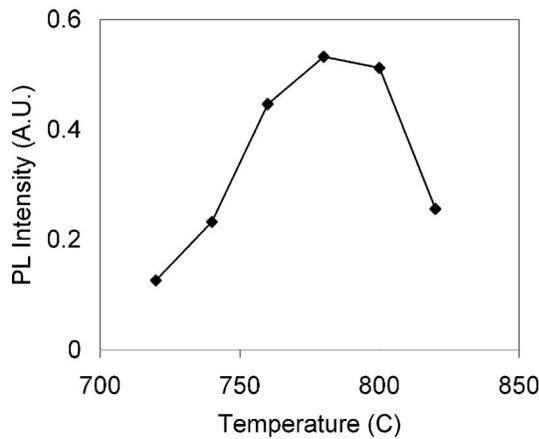


FIG. 1. PL intensity vs annealing temperature (*ex situ*, 1 min) for $\text{Ga}_{0.62}\text{In}_{0.38}\text{N}_{0.03}\text{As}_{0.943}\text{Sb}_{0.027}$ QW.

intensity initially increases and then eventually decreases when annealed too long or too hot. But unlike Fig. 1, Fig. 2 shows a very wide window of flat PL intensity, and the peak PL intensity is more than two times higher than the 1 min annealed samples. This means that all of our previous PL samples and lasers were not optimally annealed, failing to realize the full potential of GaInNAs(Sb) material. Additionally, at 700 °C, the overanneal degradation does not begin until the sample is annealed for 2 h. On the other hand, a 1 min annealing at 780 °C was enough to start degradation, as shown in Fig. 1. This implies that the overanneal degradation process has a very steep temperature dependence, or equivalently, a large activation energy. To examine this, we next annealed samples at 720 and 740 °C, until substantial degradation was observed (Fig. 2). A steep temperature dependence is indeed observed, with the degradation becoming about four times faster for every 20 °C increase, which translates into activation energy of about 7 eV, when an Arrhenius relationship is assumed.

The PL intensity improvement during the initial phase of annealing is shown to have a shallower temperature dependence. Samples were annealed at 680–720 °C, until the PL intensity improvement saturated (Fig. 3). The process is

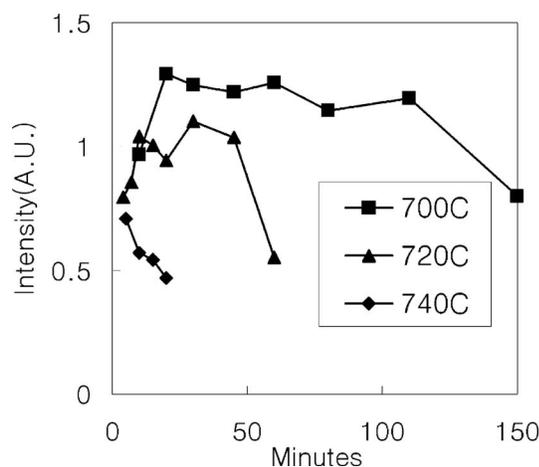


FIG. 2. PL intensity vs annealing duration for $\text{Ga}_{0.62}\text{In}_{0.38}\text{N}_{0.03}\text{As}_{0.943}\text{Sb}_{0.027}$ QW. Degradation gets about four times faster for every 20 °C increase. The optimum with 700 °C is roughly two times better than Fig. 1. Note that the PL intensity axis is, albeit arbitrary, consistent among all the figures in this report.

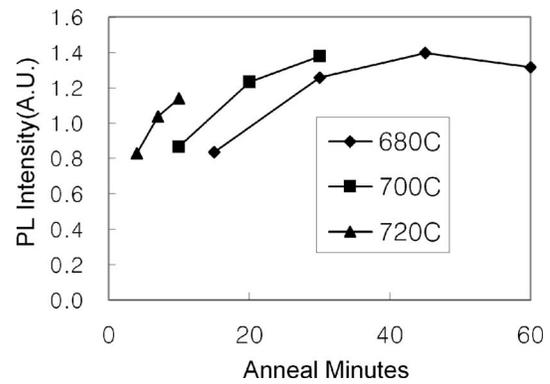


FIG. 3. PL intensity vs annealing duration for $\text{Ga}_{0.62}\text{In}_{0.38}\text{N}_{0.03}\text{As}_{0.943}\text{Sb}_{0.027}$ QW. Improvement gets about two times faster for every 20 °C increase.

about two times faster per 20 °C increase, which translates into activation energy of about 3–4 eV.

Due to this combination of a shallow temperature dependence of the improvement process and the steep temperature dependence of the degradation process, longer and cooler annealings produce better PL intensity than shorter and hotter annealings because the lower temperature inhibits the degradation process more significantly than it slows the improvement process. The optimum intensity that can be achieved with long annealings at 700 °C was indeed two times higher than that for 1 min annealings. (Compare Figs. 1 and 2.) As the best 1.55 μm GaInNAs(Sb) lasers and PL samples to date have been treated with suboptimal 1 min annealings,^{6,7,16,17} better laser performance can be expected by employing longer and cooler annealings for future laser growths.

The temperature dependence of annealing processes also holds for other GaInNAs(Sb) compositions. Two other samples with vastly different compositions and thicknesses were annealed at various temperatures for 1–80 min (Figs. 4 and 5). These samples exhibit a similar gradual temperature dependence of the PL improvement process (Fig. 4) and steep temperature dependence of the PL degradation process (Fig. 5). However, the relevant temperature ranges can be very different depending on composition (compare Figs. 2 and 5), as reported by many researchers.^{7,8,10,12,13} This implies that the activation energies of improvement and degradation processes during GaInNAs(Sb) annealing are not highly composition dependent, but the prefactors in the

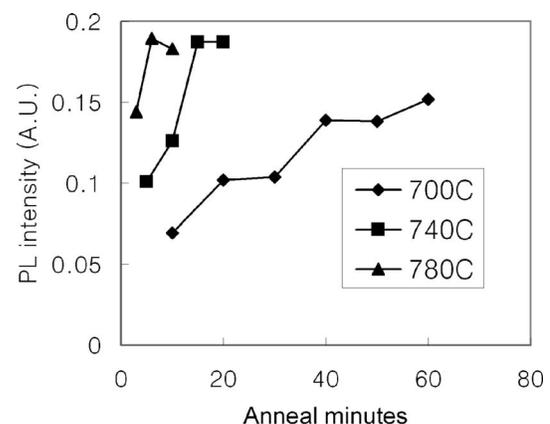


FIG. 4. PL intensity vs annealing duration for 150 nm thick, $\text{Ga}_{0.92}\text{In}_{0.08}\text{N}_{0.02}\text{As}_{0.98}$ layer. Improvement gets about four times faster for every 40 °C increase or two times faster for every 20 °C.

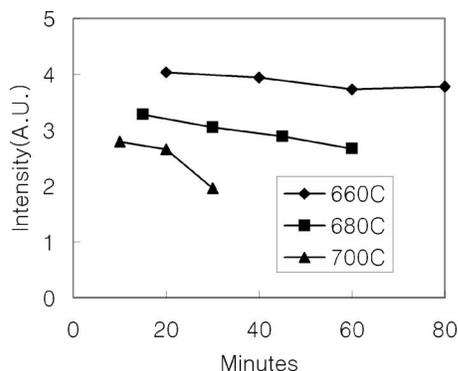


FIG. 5. PL intensity vs annealing duration for 7 nm thick, $\text{Ga}_{0.7}\text{In}_{0.3}\text{N}_{0.012}\text{As}_{0.968}\text{Sb}_{0.02}$ QW. Degradation becomes more than three times faster for every 20°C increase.

Arrhenius relation do vary with composition and strain.

In summary, we found that the intensity degradation process during overannealing has a significantly steeper temperature dependence (roughly four times per 20°C or ~ 7 eV activation energy) than the improvement process (two times per 20°C or 3–4 eV activation energy). As a result, roughly twice higher PL intensity is achieved by longer-duration, lower-temperature annealings than previously used short-duration, higher-temperature annealings. Similar trends were also identified from $\text{GaInNAs}(\text{Sb})$ samples with vastly different compositions and thicknesses, which is an interesting subject for further study. This is promising for further improvement of long-wavelength $\text{GaInNAs}(\text{Sb})$ lasers.

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