Effects of strain on the optimal annealing temperature of GaInNAsSb quantum wells

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Dilute nitride alloys have required postgrowth annealing to improve their luminescent efficiency. There exists an optimal annealing temperature that results in the highest photoluminescence intensity. Several series of GaInNAsSb samples with varying indium and antimony contents were grown to examine the effects of compositional and strain changes on this optimal annealing temperature. We show that a relationship exists between this temperature and the lattice strain of GaInNAsSb quantum wells. As strain increases in these alloys, the optimal annealing temperature decreases. Higher optimal anneal temperatures are found with lower lattice strain. This has important ramifications for the design of long-wavelength GaInNAsSb devices. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2208937]

Adding nitrogen in small concentrations to GaAs simultaneously reduces the band gap and lattice parameter,[1] contrary to the behavior of most other III-V semiconductors. With this knowledge, Kondow *et al.* added nitrogen to InGaAs to create GaInNAs.[2] This has enabled the development of GaAs-based devices operating at the telecommunication wavelengths of 1.3 μm (Refs. 3 and 4) and 1.55 μm.[5] GaInNAs has also garnered interest as the 1.0 eV junction in multijunction solar cells.[6–8] By decreasing the indium concentration from the 30%–40% mole fraction typically used for long-wavelength lasers down to 6%–8%, GaInNAs exhibits a band gap of 1.0 eV with little or no strain when grown on GaAs. Antimony has been added as a surfactant and group-V species during GaInNAs growth, improving the structural and optical qualities of the material.[9–12] GaInNAsSb devices have shown remarkable progress towards the realization of low-cost telecommunication devices with the demonstration of a very low threshold 1.55 μm edge emitting laser[13] and an electrically pumped 1.55 μm range vertical-cavity surface-emitting laser.[14] Antimony has also been utilized during GaInNAs growth for solar cell applications. With antimony, the optical quality decreases[15] while solar cell performance improves.[16] These preliminary results indicate that further investigation is required to fully understand the behavior.

Thermal annealing of dilute nitride materials is commonly performed to improve the luminescent efficiency.[17–19] This step is necessary due to the inferior quality of as-grown material. Factors including low-temperature growth and plasma damage degrade optical material quality. Typically, the photoluminescence (PL) intensity improves with increasing anneal temperatures up to a specific temperature, called the "optimal annealing temperature." For anneal temperatures hotter than this value, the PL intensity degrades until the sample is optically dead.

This curious parameter has not received much attention until it was recently found to be crucial to laser performance.[20] We present the annealing properties for three series of GaInNAs(Sb)/GaAs quantum well (QW) samples over a wide range of indium and antimony compositions. These QWs were examined for any annealing trends which may exist with different compositions and strain. Additional material analysis of these samples may be found in Ref. 15. The optimal annealing temperature is strongly correlated with strain due to compositional differences for each series of GaInNAs(Sb) samples.

The GaInNAs(Sb) single quantum well (SQW) samples used in this study were grown on *n*-type (100) GaAs substrates by solid-source molecular beam epitaxy (MBE) in a Varian Mod Gen-II system. Gallium and indium were supplied by SUMO effusion cells. A valved arsenic cracker supplied As_2 and an unvalved antimony cracker supplied antimony. According to Brewer *et al.*,[21] for the antimony fluxes utilized in this study and a cracking temperature of 850 °C, almost all antimony incident upon the growth surface should be monomeric antimony. The QWs were grown at a substrate temperature of 440 °C, measured by pyrometry. An arsenic-to-gallium overpressure of 20 times an antimony flux of $(2.0-10.0)\times 10^{-8}$ torr beam equivalent pressure (BEP) were supplied during the GaInNAsSb QW growth. Nitrogen was supplied by a modified SVT Associates plasma cell operating at a radio frequency of 13.56 MHz. Nitrogen gas of 5N (99.999%) purity was filtered through a <1 ppb (parts per billion) Pall Mini-Gaskleen purifier to minimize oxygen contamination. The plasma source was operated with 300 W input power and a nitrogen gas flow of 0.5 SCCM (SCCM density cubic centimeter per minute at STP). Compositions were measured using secondary-ion-mass spectroscopy (SIMS) and were consistent with high-resolution x-ray diffraction (HRXRD) simulations of measured spectra. Lattice strain was determined from HRXRD. All samples were annealed *ex situ* in a N_2 ambient with a GaAs proximity cap at various temperatures for 1 min. PL was obtained at room temperature with an argon-ion laser.

GaInNAs(Sb) QWs containing 34% indium and 2.3% nitrogen were grown using antimony fluxes of 0, 2×10^{-8}, 6×10^{-8}, and 1×10^{-7} torr BEP. Strain values for the four samples are listed in Table I. The GaInNAs sample which was grown with no antimony exhibited severe material degradation and a strain value could not be reliably obtained. Strain values for the other three samples were determined to

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TABLE I. A summary of the in-plane strains for GaInNAsSb/GaAs QWs, with varying antimony and indium concentrations, as determined by HRXRD. Antimony fluxes, rather than antimony concentrations, are listed since the concentrations depended upon the indium concentration due to incorporation interplay between the two elements.

Sb BEP (torr)	8% In	16% In	24% In	32% In
0 Sb	0.24%			N/A
2.0×10^{-8}	0.27%			2.0%
6.0×10^{-8}	0.42%			2.0%
1.0×10^{-7}	0.62%	1.1%	1.6%	2.0%

be 2.0%. The small increase in antimony content from 0.5% to 2.0% in these samples did not change the strain appreciably. Figure 1 shows the annealing properties of the four samples in this series. The GaInNAs (no antimony) sample had extremely poor optical quality for all anneal temperatures, consistent with the poor as-grown material quality, while the three GaInNAsSb samples displayed much higher PL intensities. The optimal annealing temperatures for these three samples were all found to be identical at 800 °C. From this set of samples, the lack of shift in the optimal annealing temperature is concurrent with the lack of change in lattice strain.

To investigate the effects on the optimal annealing temperature of samples with different strain values due to varying antimony compositions, another set of GaInNAs(Sb) QWs was examined. For these samples, the indium content was lowered to 8%–10% and the antimony concentrations were modulated between 0% and 5.4%. Reducing the indium concentration in GaInNAs(Sb) for solar cell applications is required to decrease the lattice strain, enabling several micron-thick layers. Figure 2 shows the PL intensities of these QWs obtained at each annealing temperature. It is seen that the antimony-free sample has the highest PL intensity with an optimal anneal temperature of ~850 °C. With increasing antimony concentrations, the optimal anneal temperature shifts downwards to 820 °C for the GaInNAsSb QW with 5.4% antimony. Larger antimony concentrations in these samples led to higher strain values, ranging from 0.24% with no antimony and 0.62% with 5.4% antimony concentration. As the antimony content and lattice strain increased in each sample, the optimal annealing temperature correspondingly decreased.

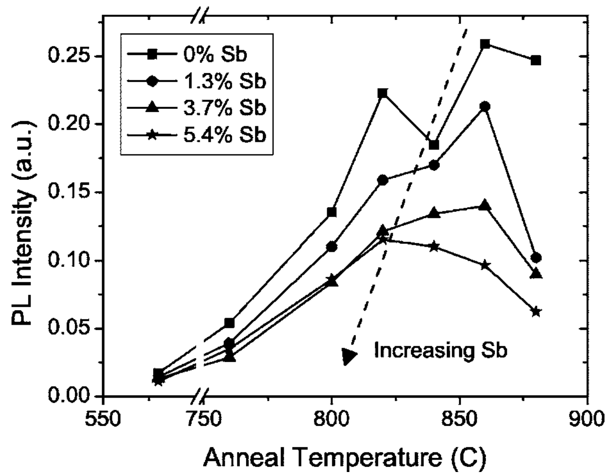

FIG. 2. PL intensity plotted against different anneal temperatures for GaInNAs(Sb) QWs. These samples contained 8%–10% indium and 0%–5.4% antimony content.

A third set of GaInNAsSb samples with varying indium content was investigated to rule out the possibility that an increase in antimony concentration, rather than lattice strain, was the primary reason for lower optimal annealing temperatures. For these samples, even though the antimony flux was held constant during growth, the antimony concentration dropped from 7.5% to 0.8% when the indium concentration was increased from 8% to 32%. Even though a drop in antimony concentration by itself leads to a strain reduction, the change in indium content was large enough to increase the strain from 0.62% to 2.0%. Figure 3 displays the PL intensities of these GaInNAsSb samples with various anneal temperatures. The optimal anneal temperature of the GaInNAsSb sample with 8% indium content could not be determined due to a lack of wafer material but appears to be greater than 850 °C. With larger indium concentrations, the PL intensity increases and the optimal anneal temperature shifts downwards to 760 °C for a sample with 32% indium content. This large shift in optimal anneal temperature also correlates with a large change in lattice strain. A reduction in antimony concentration with decreasing optimal anneal temperatures also

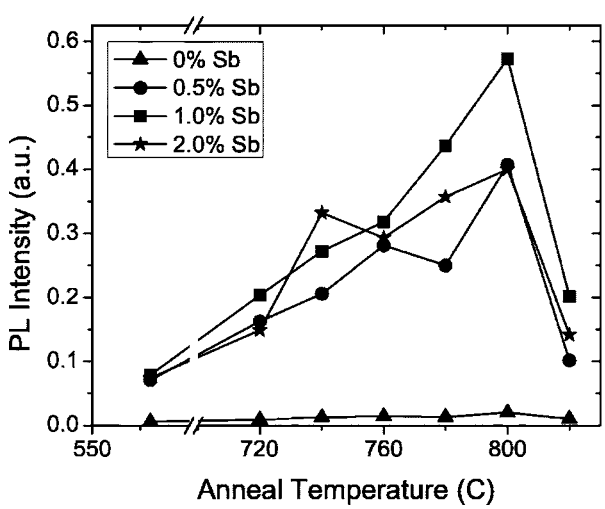

FIG. 1. PL intensity as a function of different annealing temperatures for GaInNAs(Sb) QWs. These samples contained 32%–34% indium and 0%–2% antimony content.

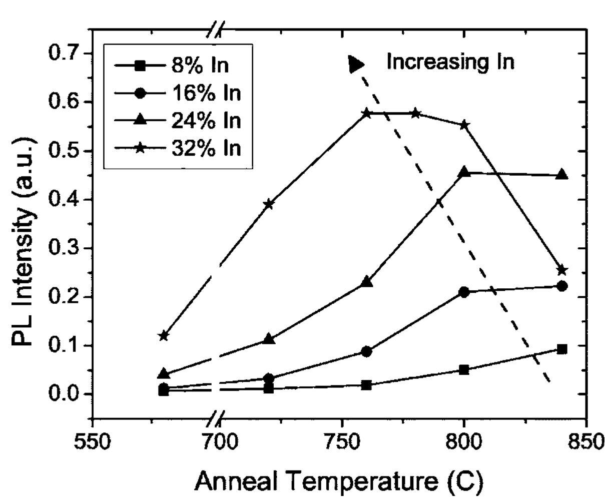

FIG. 3. PL intensities of GaInNAsSb QWs as a function of different annealing temperatures. These samples were grown under constant antimony flux while the indium concentration was varied from 8% to 32%.

shows that antimony itself does not have a direct effect.

The annealing study results from the three sets of GaInNAsSb QWs indicate a relationship between lattice strain and the optimal anneal temperature. In both cases where the GaInNAs(Sb) QW strain was varied, the optimal anneal temperature decreased with larger lattice strain values. The magnitude of the strain shift also appears to affect the shift in optimal anneal temperature. The samples consisting of 6%–8% indium and varying antimony content only had a 30 °C decrease with an increase in strain of 0.38%. For the sample under constant antimony flux during growth but varying indium content, a >90 °C decrease in the optimal anneal temperature was observed for an increase in strain of 1.38%. The set of GaInNAsSb samples that had no change in strain correspondingly exhibited no variation in the optimal anneal temperature. The individual atomic species themselves do not appear to be a primary cause of the shift in optimal anneal temperature. In another study, the optimal annealing temperature was observed to have remained the same with higher nitrogen concentration.[20] While strain is the dominant factor in shifting the optimal anneal temperature, there are undoubtedly additional influences which will affect the optimal annealing temperature. For example, altering important growth conditions such as rf plasma operation will affect, to a certain extent, the optimal anneal temperature. In this article, all samples were grown under mostly identical growth conditions to eliminate any of these effects.

The physical cause of the decrease in optimal anneal temperature with strain is unknown and requires further study. It is suspected that dilute nitride materials which are highly strained have lower activation energies for defect formation or propagation. Lower temperatures are required to provide sufficient thermal energy to initiate material degradation. The type of defect is also unclear, although phase separation or misfit dislocation formation is proposed. Strain cannot predict the absolute location of the optimal anneal temperature as other important factors, such as material quality, growth conditions, and layer structure, must be considered. However, materials with larger lattice strain result in lower optimal anneal temperatures and vice versa.

These findings have important implications for the growth of dilute nitride lasers. Growth of edge emitting lasers involves a top cladding layer, and vertical-cavity surface-emitting lasers require a distributed Bragg reflector (DBR) above the active region. These thick layers consisting of AlAs/GaAs layers have optimal growth temperatures of 580–610 °C and above. For materials with low optimal anneal temperatures, the prolonged growth at high temperature of the top cladding or DBR layers can effectively overanneal[20] the active region by exceeding an effective "thermal budget" and lead to poor performance. GaInNAsSb with higher optimal anneal temperatures is able to withstand the *in situ* annealing during top cladding growth and do not suffer from annealing-related degradation.

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