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Selective modification of band gap in GaInNAs/GaAs structures by quantum-well intermixing

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We report an investigation of selective quantum-well intermixing (QWI) in 1.3- μm GaInNAs/GaAs multi quantum wells by silica-cap-induced disordering processes. After thermal annealing under specific conditions, controlled shifts of band gap at room temperature of over 200 nm have been observed in sputtered SiO_2 -capped samples, while uncapped and SiO_2 -capped samples by plasma-enhanced chemical vapor deposition demonstrated negligible shift. This selective modification of the band gap in GaInNAs quantum wells has been confirmed by detailed photoluminescence and photoluminescence excitation spectroscopy, and by secondary ion mass spectrometry. The controlled tuning of the band gap of GaInNAs/GaAs by QWI is important for a wide range of photonic integrated circuits and advanced device applications. © 2003 American Institute of Physics. [DOI: 10.1063/1.1583865]

In recent years, dilute nitride alloy III-V semiconductors have attracted a great deal of attention. The incorporation of a small amount of nitrogen into GaAs-based materials, especially InGaAs, gives rise to physical properties favorable for optoelectronic devices in optical fiber communications.¹ Various devices operating near 1.3- μm wavelength based on GaInNAs/GaAs quantum wells (QWs) have been demonstrated, including edge-emitting lasers,² vertical-cavity surface-emitting lasers (VCSELs),³ multijunction solar cells,⁴ and saturable Bragg reflectors for mode-locking.⁵ To extend the applications of this technologically important material system, particularly towards integrated multifunction devices and photonic integrated circuits, spatially-controlled modification of the band gap is required. To this end, quantum-well intermixing (QWI) techniques offer a powerful approach,⁶ as has been successfully demonstrated in various materials systems, such as InGaAsP/InP, AlInGaAs/InP, and GaAs/AlGaAs.^{6–8} In particular, the approach of enhanced interdiffusion using sputtered silica caps has proven very attractive.^{6,8}

It is highly desirable to extend QWI techniques to GaInNAs/GaAs structures; however, this is especially challenging due to the complicating effects of the thermal annealing required to activate efficient luminescence in this material system. Sample-dependent photoluminescence (PL) shifts of tens of nm^{9–19} are associated with this process, whether carried out *in situ* or post-growth, and the associated mechanisms are complicated and remain under debate.^{9–19}

This uncontrolled “natural” band gap variation induced by thermal annealing is not desirable for practical applications and can easily mask the details of QWI effects. Here, we investigate controlled QWI utilizing silica cap-induced disordering processes. To address these issues, we study well-characterized GaInNAs QW material already proven to be the basis of high-performance diode lasers and VCSELs, and ensure that the material has been annealed “to saturation” before the disordering processes are studied. After rapid thermal annealing (RTA) at 700 °C for ~ 180 s, controlled shifts in band gap at RT of up to 200 nm have been observed in sputtered SiO_2 -capped samples, while uncapped and by plasma-enhanced chemical vapor deposited (PECVD) SiO_2 -capped samples demonstrated negligible shift. This QWI of GaInNAs QWs has been characterized by detailed PL and PL excitation (PLE) spectroscopy, and by secondary ion mass spectrometry (SIMS).

The GaInNAs/GaAs multi QW (MQW) structures investigated are from a series of samples used in our earlier detailed studies of electronic states, band-offsets, and localization effects,^{20,21} and were grown by solid-source molecular-beam epitaxy on GaAs (001) substrates. The five-period MQWs were sandwiched between two five-period AlAs (2-nm)/GaAs (2-nm) superlattice cladding layers. The samples were *in situ* annealed at 750 °C to activate efficient luminescence and to saturate the PL blueshift; thus, the measured PL characteristics of the as-grown samples are already the result of one annealing step. The sample structure studied here has a well width of 7 nm and RT PL is centered at about 1321 nm. The material was cleaved into samples ~ 3 mm $\times$ ~ 3 mm, each of which was characterized by PL and PLE before

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FIG. 1. Evolution of PL spectra of sputtered SiO₂-capped GaInNAs/GaAs MQW samples annealed at different conditions.

further processing. Samples were then left either uncapped (for reference) or coated with ~ 50 -nm-thick SiO₂ capping layers deposited by either PECVD or sputtering. RTA was then performed in a rapid thermal processing system.⁶ During the processing, the samples were kept in flowing nitrogen ambient, and a silicon or GaAs wafer covered the surface to protect the samples. For brevity, we refer to the samples receiving no *post-growth* annealing as “nonannealed,” although all samples discussed have been subjected to the same *in situ* annealing step.

Figure 1 shows typical RT PL spectra, comparing as-grown (nonannealed) characteristics with those of sputtered SiO₂-capped samples annealed at different temperatures for 180 s. Without thermal annealing, the sputtered SiO₂-capped sample has the same PL peak position and line shape, but the intensity shows an apparent decrease, which is ascribed to increased loss due to the defects at the interface generated by the bombardment of the sputtering process. Upon high-temperature annealing, the PL peak shifts to the shorter wavelength substantially. As a specific example, the 700 °C annealed sample has a PL blueshift of about 203 nm, and the linewidth increases from 46.8 to 49.3 nm. This large blueshift is clearly sufficient for broad application to optoelectronic devices. Full systematics of PL blueshift with the annealing conditions (temperature and time) have been obtained in a 9-nm QW sample with similar composition from the same growth series,²² where more material was available. The blueshift increases in a controlled manner with temperature and annealing time, consistent with the features expected of an interdiffusion process. Systematic tests have shown that the band-gap shift induced by the RTA is highly reproducible. The fact that true QWI has taken place is demonstrated by the following results.

In Fig. 2, we compare the RT spectra of a nonannealed sample and samples with same annealing conditions (700 °C for 180 s) but different capping processes. Compared with the nonannealed reference sample (a), the annealed sample without capping (b) shows negligible blueshift of ~ 5 nm, demonstrating that the prior *in situ* annealing has indeed achieved saturation of the “natural” blueshift commonly observed. Furthermore, it is noticeable that the sample capped with PECVD SiO₂ (c) shows only a very small ~ 9 -nm shift.

FIG. 2. Normalized PL spectra of GaInNAs/GaAs MQW samples with different capping annealed under the same conditions of 180 s at 700 °C. Spectra (b) and (c) are vertically offset for clarity.

However, in marked contrast to (a)–(c), the sample capped with sputtered SiO₂ (d) shows a blueshift of ~ 203 nm. This is consistent with the behavior shown by other materials under such capping experiments.⁶

The PLE spectra of the same four samples have been measured at 10 K, as shown in Fig. 3. Similar to the PL results, the lowest transition energies in the PLE spectra of the uncapped sample and PECVD SiO₂-capped sample increased by only ~ 0 and 5 meV, respectively, compared to the unannealed sample. However, the lowest transition energy of the sputtered SiO₂-capped sample increased by about 190 meV. These spectra provide direct evidence that the PL blueshift is correlated with the increase of the lowest transition energy (e1–hh1) in the QWs, and only takes place with sputtered SiO₂ capping. The reduced strength of the lowest energy exciton absorption peak in the sputtered SiO₂-capped sample may be attributed to inhomogeneous broadening associated with the diffusion fluctuation in different QWs.

To further elucidate the substantial increase of the transition energy in the sputtered SiO₂-capped sample, SIMS analysis of the compositional profile of the above samples

FIG. 3. PLE spectra of GaInNAs/GaAs MQW samples with different capping annealed under the same conditions of 180 s at 700 °C.

FIG. 4. SIMS results for (1) the PECVD SiO₂-capped GaInNAs/GaAs MQW sample, and (2) the sputtered SiO₂ capped GaInNAs/GaAs MQW sample after annealing at 700 °C for 180 s.

was undertaken. Figure 4 shows the In and Ga composition profiles for annealed samples covered with PECVD (thin curves) and sputtered (thick curves) SiO₂. Measurements of N concentration were also taken, but for clarity are not shown here. The five QWs and barriers can be clearly seen by the sharp change of both In and Ga composition with depth. No evidence of interdiffusion is seen in the PECVD SiO₂-encapsulated sample. This is confirmed by the small blueshift of PL and the contrast in Ga composition between barriers and wells. The measured composition of In and N in the QWs and the layer thickness are consistent with the nominal values determined previously by high-resolution x-ray diffraction.

By contrast, in the sputtered SiO₂-encapsulated sample (thick curves), interdiffusion of In and Ga between the QWs and the barriers is clearly apparent; the profiles change shape and the compositions of In and Ga change accordingly. The composition change in the QWs is compensated by the corresponding changes in the adjacent barriers. It should be noted that there was no observed change of N composition in the two samples just described, and the N composition in the QWs, as determined by this technique, is the same as in the nonannealed sample. This suggests that the diffusivity of N–As is very small and cannot account for the QWI. A detailed calculation of the increase of transition energies related to the composition and potential profile change is difficult to undertake, and work is still underway to facilitate this. As an estimation, however, taking into account the In composition change from 0.38 to 0.25, the band gap of bulk GaInNAs should increase by about 165 meV.²³ This is reasonably consistent with the observed 190-meV increase of the lowest transition energy in QW determined by low-temperature PLE. Therefore, our results provide very clear evidence that the PL blueshift has originated from the QWI effect, due mainly to the interdiffusion of In–Ga between the QWs and barriers. It is believed that the driving force of enhanced interdiffusion in the sputtered SiO₂-capped samples originates from the generation of increased point defects by ion bombardment during the sputtering process.²⁴ Although the detailed diffusion mechanism in this case needs further in-

vestigation, we have shown, consistent with the behavior of other materials,⁶ that the differential effects of sputtered and PECVD silica caps can be used to control the band gap.

In conclusion, we have reported on the investigation of controlled QWI in 1.3-μm GaInNAs/GaAs MQWs. By applying sputtered SiO₂ capping and suitable rapid thermal annealing, a blueshift of PL wavelength over 200 nm has been achieved, while negligible blueshift was observed in PECVD SiO₂-capped or noncapped samples. The selective modification of the band gap of GaInNAs/GaAs by QWI is important for a wide range of photonic integrated circuit and advanced device applications. Photoluminescence excitation spectra and secondary ion mass spectrometry have confirmed that the band-gap tuning mechanism results from the interdiffusion of In–Ga between the quantum wells and the barriers.

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