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Role of Sb in the growth and optical properties of 1.55 μm GaInN(Sb)As/GaNAs quantum-well structures by molecular-beam epitaxy

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High-quality GaInN(Sb)As/GaNAs double quantum wells (QWs) which emit at 1.54 μm wavelength at room temperature with a narrow linewidth of ~ 34 meV (12 meV at 5 K) were fabricated by molecular-beam epitaxy on GaAs substrates. Photoluminescence and photoluminescence excitation spectroscopy were used to study the electronic states and optical properties of these heterostructures. By characterizing samples grown using different fluxes of Sb, the role played by Sb in the growth process and optical properties was elucidated. At low Sb flux, Sb atoms act mainly as a surfactant which improves the microstructure of the QWs and enhances the photoluminescence intensity. With an increase of Sb flux, some of the Sb atoms may incorporate into GaInNAs to form a quinary compound. In the latter case, the incorporation of Sb could also enhance the N composition in the QWs, which may be responsible for the further reduction of the band gap. © 2005 American Institute of Physics. [DOI: 10.1063/1.2123383]

Dilute nitride compound semiconductors and related heterostructures have received considerable attention in the last decade due to their intriguing physics and potential applications in 1.3–1.55 μm optoelectronic devices.¹ Various devices with attractive performance around 1.3 μm have been demonstrated using compressively strained GaInNAs/GaAs quantum wells (QWs) as active materials.^{2–5} Recently, a great deal of effort has been paid to extending the emission wavelength of this material system towards 1.55 μm . However, this is challenging because further reduction of the band gap in GaInNAs requires the increase in composition of In and/or N, risking a serious deterioration of the optical quality. This challenge arises from either the larger strain as the In content increases or the increase in nonradiative recombination centers as the N content increases. Furthermore, strong phase separation may occur with the increase of N and In contents.^{6,7} The introduction of strain-compensated GaNAs layers between GaInNAs and GaAs appears to be an effective approach to relieving the difficulty,⁸ but for 1.55 μm structures the increased stress at the interface between GaNAs and GaInNAs has proven unfavorable for the interface quality.⁹ Additional insertion of strain-mediated GaIn(N)As layers is feasible for the improvement of interface quality and photoluminescence efficiency,^{10,11} but this again increases the total compressive strain in the whole structure and is thus undesirable for the growth of multi-QWs. Recently several groups have employed antimony as a surfactant to assist the growth of GaInNAs and succeeded in the realization of 1.55 μm photoluminescence (PL) and lasing at room temperature,^{12–15} but there has been very little investigation into the effect of Sb on the optical and structural properties. In this letter we report detailed characterization on this novel material system with different amounts of Sb, using PL and PL excitation (PLE) spectroscopy. As PLE measures the intrinsic transitions of the QWs, this combined

investigation with PL offers insight into the role played by Sb in the growth process and optical properties.

The samples were grown on n^+ -GaAs substrates by molecular-beam epitaxy in a custom V90 system, using Ga, In, and Al thermal effusion cells and valved cracker cells for As₂ and Sb₂. Active N was provided by a radio frequency plasma source using N₂/Ar dynamic gas switching.¹⁶ The basic double-QW (DQW) structure consists of 7 nm Ga_{0.6}In_{0.4}N_yAs_{1-y-z}Sb_z QWs and 20 nm GaN_{0.045}As_{0.955} barriers, where the nominal N content y is $\sim 2.7\%$. In this study, we focus on three samples with Sb flux of 0 (sample V255), 0.012 mL/s (sample V259) and 0.028 mL/s (sample V260), respectively. The growth conditions of these three samples are identical except for the Sb flux. Before the growth of the DQWs, a 100 nm GaAs buffer layer was deposited first and then a 20 period GaAs (2 nm)/AlAs(2 nm) superlattice followed by 251 nm GaAs. After the growth of the DQWs, the samples were capped by a layer of 100 nm GaAs, followed by 50 nm Al_{0.33}Ga_{0.67}As and 50 nm GaAs. The growth temperatures were 415 °C for the active region and 600 °C for the remainder of each structure. The samples were annealed at 700 °C in a nitrogen atmosphere for 5 min with GaAs proximity capping. The PL measurements were carried out using excitation by a frequency-doubled Nd:yttrium-aluminum-garnet laser (532 nm), and detection by a 0.46 m grating monochromator using standard lock-in techniques. The light source for PLE was provided by a 250 W tungsten-halogen lamp combined with a 0.27 m grating monochromator and suitable filters. The detector used in these experiments was a thermoelectrically cooled InGaAs detector.

Figure 1 shows the PL spectra of the three samples at 5 and 300 K, respectively. The 300 K PL peak of the sample (V255) without Sb in the QWs is at around 1511 nm. When a small amount of Sb is incorporated into the QWs (V259), the PL at 300 K demonstrates negligible shift, but the PL intensity increases about 2.5 times and the PL linewidth decreases from 45 to 33 meV. With further increase of Sb composition, there appears a pronounced ~ 30 nm redshift of

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FIG. 1. PL spectra of three samples V255, V259, and V260 measured at 300 K (upper panel) and at 5 K (lower panel).

the PL peak (the peak wavelength at 300 K is as long as 1541 nm, very close to the desired $1.55 \mu\text{m}$). The PL intensity of V260 decreases, and the emission linewidth increases, only slightly compared to sample V259. The optical quality of sample V260 is apparently better than V255 as far as the PL intensity and linewidth are concerned. The PL linewidth of V260 reduces from 34 meV at 300 K to 12 meV at 5 K, which represents the very high quality of the dilute nitride structures in this wavelength range.

Figure 2 plots the PL and PLE spectra of all three samples, where the typical absorption profiles characteristic of QWs can be seen. Apart from the absorption of the GaAs and GaNAs barriers, three transition features associated with the QWs can be observed, readily assigned to E_1-HH_1 , E_1-LH_{barrier} , and E_2-HH_2 transitions, respectively.¹⁴ The type II transition of E_1-LH_{barrier} is due to the higher energy level of light holes in the GaNAs barriers lifted by the tensile strain than that of the compressively strained QWs.¹⁴

To gain insight into the effect of Sb on the electronic states, we compare the PLE spectra of these three samples by normalizing at the barrier transition region as shown in Fig. 3. It is interesting to examine the evolution of the PLE pro-

FIG. 2. PL and PLE spectra of the three samples measured at 5 K, with identified transitions indicated.

FIG. 3. Comparison of the PLE spectra of the three samples normalized with respect to the barrier absorption. The curve of V255 is vertically shifted for clarity.

file in the QW absorption region with increase in the Sb flux. For sample V255 in which no Sb is introduced, the PLE displays a very sharp edge at E_1-HH_1 transition, which is typical of a type I QW. Normally, this transition edge is correlated with the quality of the QWs: the better the QW quality, the sharper the transition edge. As can be seen from the PL measurements shown in Fig. 1, the optical properties have been improved by the introduction of Sb, which suggest that as a surfactant, Sb atoms play a role of increasing the structural quality of the QWs. On the contrary, the PLE profiles seem to demonstrate an abnormal trend: the addition of Sb gives rise to an absorption tail at the lowest transition edge. We tentatively attribute the earlier-mentioned “anomaly” to the influence of Sb on the energy profile across the QWs. As is well known, as a surfactant, Sb atoms tend to segregate to the surface during the growth.¹² It turns out that there is a very thin layer enriched with Sb at the interface of QW and barrier. This thin layer should have different energy gap from the quantum wells and therefore the resultant energy profile in the whole structure is actually modified. We propose this modified energy diagram as shown in the inset of Fig. 3 by taking into account that replacing the As with Sb mainly lifts the valence energy.¹⁷ Apparently, in this case, the conduction band has been barely changed. However, there exist bound states in the valence band localized at the interface. For the optical absorption revealed by the PLE spectrum, the transitions from these localized valence states to first extended electronic state (E_1) will lie at the lower energy side of quantized QW transition (E_1-HH_1), which can explain the absorption tail appearing in the PLE spectra of samples V259 and V260.

In order to further investigate the effect of Sb on the optical properties of GaInN(Sb)As/GaNAs QWs, we performed PL measurements as a function of excitation intensity. Figure 4 shows the dependence of the PL spectra on the excitation intensity for samples V255 and V260, respectively, measured at 5 K. It is noted that for an excitation intensity change of three orders of magnitude, sample V260 displays a gradual PL shift to higher energy (total shift about 5 meV) while the PL in V255 has barely shifted. Sample V259 demonstrates a similar trend to V260 but is not shown here. In a normal nitride QW, an excitation-intensity-induced PL blueshift at low temperature is considered to be related to the filling of localized states induced by the fluctuation of N contents in the QW plane,¹⁸ and the amount of blueshift

FIG. 4. PL spectra of sample V255 (upper panel) and V260 (lower panel) at various excitation powers measured at 5 K.

should depend on the distribution of the localized states and the excitation range. The absence of blueshift in V255 actually implies that the localized states are distributed mainly close to edge of E_1-HH_1 and our highest excitation intensity is not strong enough to saturate these localized states. With the introduction of Sb, the surfactant effect should further improve the structural quality of the QWs and reduce the localization energy induced by the fluctuation of N distribution. Therefore the observed blueshift in V259 and V260 cannot be attributed to the saturation of localized states induced by N fluctuation in the QWs, but rather should be related to energy diagram modified by Sb at the surface layer,¹⁹ which is consistent with the absorption tail observed by PLE spectra.

Returning to Fig. 3, the QW absorption features of V255 and V259 are almost the same except for the tail below the E_1-HH_1 transition edge revealed in the spectrum of V259. This is in agreement with the room temperature PL observation and strongly indicates that Sb atoms have not been incorporated uniformly into the quantum wells but rather are left at the surface. However, in V260, both PL and PLE have been changed pronouncedly, which can be attributed to the incorporation of Sb into the lattice of GaInNAs. We notice that the energy difference in E_1-LH_{barrier} transition between V255 and V260 is ~ 13 meV, which means that E_1 energy level in V260 has been decreased by 13 meV compared with V255. Although the energy of E_1-HH_1 transition in V260 cannot be derived precisely from the low temperature PLE spectrum due to the absorption tail, we can estimate the energy difference of E_1-HH_1 transition between V255 and V260 from the room temperature PL peaks to be about 16 meV. Therefore the energy change of HH_1 in V260 is only 3 meV. In consideration that the effects of adding a small amount of N and Sb into the GaInAs are mainly decreasing the conduction band and increasing the valence bands, respectively, we conclude that while the energy gap reduction in V260 is partly due to the incorporation of Sb into GaInNAs, the main reason should be attributed to the increased N content. Another evidence for the N incorpora-

tion comes from the absorption strength just above the E_1-HH_1 transition. As can be seen from Fig. 3, the absorption strength of V260 is apparently lower than V255, while V259 is the same as V255. It has been shown theoretically that the incorporation of N into the lattice of InGaAs will decrease the transition matrix element due to the strongly localized wave function induced by N atoms.²⁰ Therefore Fig. 3 offers further evidence that more N atoms have been incorporated into V260.

In conclusion, the effect of employing Sb during the growth of GaInNAs/GaNAs QWs on the optical properties has been investigated by detailed PL and PLE spectroscopy. Evidence shows that at low flux, Sb acts as a surfactant which improves the structural quality of the QW but remains on the surface of the QW. With the increase of Sb flux, some of the Sb atoms are incorporated into the lattice of GaInNAs to form a quinary compound. Moreover, the incorporated Sb atoms enhance the N content, which is responsible for the further reduction of the band gap. This complicated incorporation profile is consistent with our detailed analysis on structure and composition.²¹

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