Critical parameters for the molecular beam epitaxial growth of 1.55 μm (Ga,In)(N,As) multiple quantum wells

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The authors discuss the effect of substrate temperature and As beam equivalent pressure (BEP) on the molecular beam epitaxial growth of (Ga,In)(N,As) multiple quantum wells (MQWs). Transmission electron microscopy studies reveal that a low substrate temperature essentially prevents composition modulations. Secondary ion mass spectrometry results indicate that a low As BEP reduces the incorporation competition of group V elements. The low substrate temperature and low As BEP growth condition leads to (Ga,In)(N,As) MQWs containing more than 4% N preserving good structural and optical properties, and hence demonstrating 1.55 μm photoluminescence emission at room temperature. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2372760]

Dilute nitride (Ga,In)(N,As) quantum wells (QWs) grown on GaAs are promising materials for low-cost, high-performance semiconductor lasers emitting at the 1.3–1.55 μm optical fiber telecommunication wavelength.[1,2] Those devices have been fabricated by molecular beam epitaxy (MBE). Research activities over the recent years have resulted in edge-emitting as well as vertical cavity surface-emitting lasers operating near 1.5 μm.[3,4] The introduction of large amounts of In ($\geqslant 30\%$) and N ($\geqslant 3\%$) into the (Ga,In)(N,As) QWs is required for the emission above 1.5 μm. However, this enhances the phase separation tendency stemming from the inherent large miscibility gap,[5,6] which makes the growth of high-quality epitaxial layers difficult.[7] To overcome the difficulties, a surfactant-mediated growth using Sb has been suggested as a possible solution.[2,3] On the other hand, several groups have recently reported emission beyond 1.5 μm from (Ga,In)(N,As) QWs without using Sb, using specific growth conditions. Those conditions are characterized by a lower substrate temperature T_s and a lower As beam equivalent pressure (BEP),[4,8,9] compared to the commonly used T_s of 420–450 °C with V/III BEP ratios R_{BEP} of 15–20.[2,3] In general, the growth processes of this materials system have not yet been well understood.

In this letter, we investigate the effect of the substrate temperature and the As beam equivalent pressure on the growth of (Ga,In)(N,As) multiple quantum wells (MQWs), revealing the significance of the simultaneous adjustment of these two parameters in order to obtain 1.55 μm emission.

All the samples were grown on semi-insulating GaAs (001) substrates by MBE. Conventional solid-source effusion cells were used for Ga and In. The As was supplied by a valved cracker cell operated in the As_4 mode, which allows a precise control of the As BEP during the growth. Nitrogen was supplied by a rf plasma source. T_s during growth was monitored with a thermocouple.[8] For the growth of the MQWs, the fluxes of Ga, In, and N were fixed throughout this study. The In content was kept at 36%, and the N concentration was kept at about 4% by assuming an identical incorporation for the ternary and quaternary materials. The growth rate for the (Ga,In)(N,As) QWs was 0.4 μm/h. The Ga(N,As) barriers were grown by closing the N source shutter. However, about 0.8% N was incorporated into the barrier layers, since a small amount of atomic N surpasses the closed shutter. R_{BEP} was varied by changing the As BEP, where the As BEPs of 4.3×10^{-7} and 7.1×10^{-6} Torr correspond to R_{BEP} of 3 and 50, respectively. The atomic V/III flux ratio R_{atom} was estimated from the reflection high-energy electron diffraction (RHEED) transition points between group III rich and As rich conditions at temperatures between 375 and 580 °C, performing an experiment similar to that of Riechert *et al.*[10] We thereby deduced an empirical relation $R_{BEP}\approx 1.8R_{atom}$, which should be applicable for the temperatures used in this study (320 °C $\leqslant T_s \leqslant$ 450 °C).

The layer sequence of the samples is depicted in Fig. 1. Sample A consists of 19 QWs divided in six series grown under a fixed R_{BEP} of 5, with varying T_s between 320 and 450 °C. Sample B consists of 15 QWs divided in five series grown at a constant T_s of 375 °C but under different R_{BEP} ranging from 3 to 50. In order to adjust the values of the growth parameters for each series of the QWs, we carried out growth interruptions at the Ga(N,As)/(Ga,In)(N,As) interface just before the growth of the first QW of each series. During the growth interruptions, we varied T_s (for sample A) or R_{BEP} (for sample B), and then waited several minutes until the conditions were stabilized before restarting the growth. As shown later, this growth interruption does not affect the structural perfection of the interfaces.

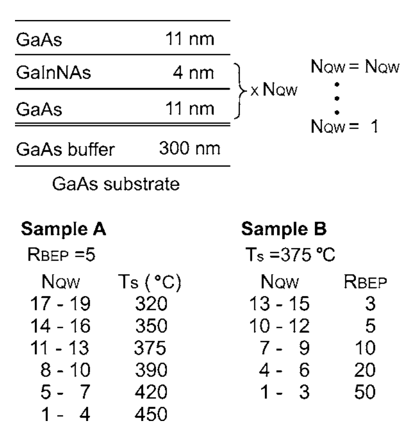

FIG. 1. Schemes of sample A and sample B. N_{QW} denotes the numbers of QWs. The growth conditions for each series of QWs are mentioned.

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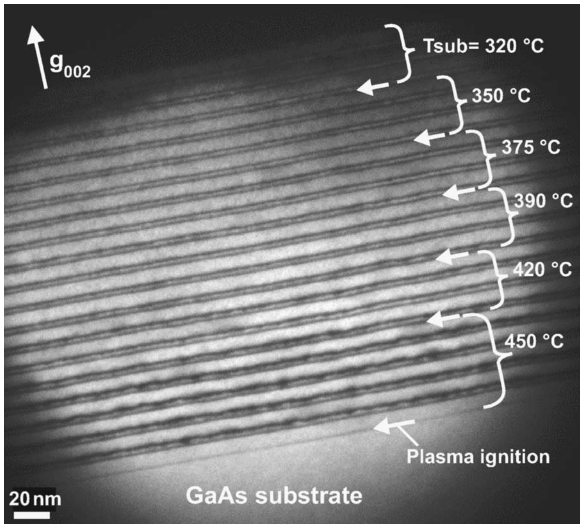

FIG. 2. Cross-sectional dark-field TEM micrograph ($\mathbf{g}=002$) of sample A. Growth interruptions before the growth of the first QW of each series are indicated by arrows.

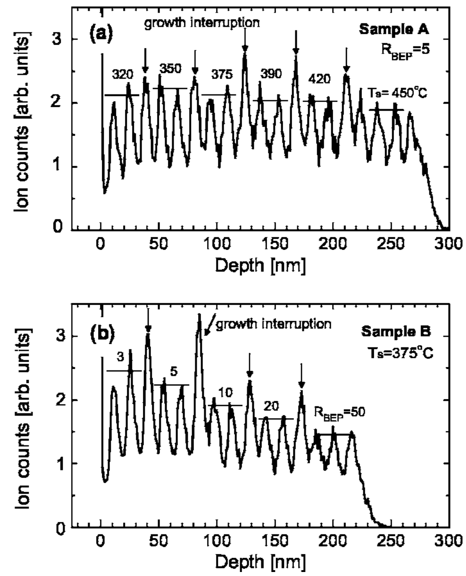

FIG. 3. SIMS depth profiles of N for (a) sample A and (b) sample B. The interfaces at which the growth interruptions were carried out are indicated by arrows. Varied parameters, T_s or R_{BEP}, are mentioned for each series of QWs. The parallel bars represent the averaged peak heights of the corresponding QWs for each series.

The structural/morphological properties were investigated by cross-sectional transmission electron microscopy (TEM). The structural and compositional properties were determined by high-resolution x-ray diffraction (XRD) with a simulation based on the dynamical diffraction theory.[11] The growth front was monitored *in situ* by RHEED. Depth profiles of N were obtained by secondary ion mass spectrometry (SIMS) employing Cs^+ primary ions with an impact energy of 5.5 keV. The optical properties were investigated by photoluminescence (PL) using a He–Ne laser and a cooled Ge detector. The measured PL spectra were corrected for the system response.

First, we investigate the effect of T_s on the growth front at $R_{\text{BEP}}=5$. Figure 2 shows a dark-field cross-sectional TEM image of sample A, obtained with $\mathbf{g}=002$ imaging condition which is sensitive to the chemical composition of zinc-blende compound semiconductors.[7] Note that the bottom-side interfaces of all the QWs are smooth without showing detectable degradations, including the interfaces at which the growth interruptions were carried out. The smoothness was also confirmed by the observation of preserved bright and streaky RHEED patterns.[12] We hence conclude that the growth interruptions insignificantly degrade the structural properties of the bottom-side interface of the first QW for each series, and the latter grown QWs are not affected by it.

Roughening of the upper interfaces and strong contrast modulations can be clearly observed for the QWs grown at T_s of 420 and 450 °C. Apparently, these features are more pronounced for the QWs grown at the higher temperature of 450 °C. The relaxation of epitaxial strain, however, does not yet occur since no misfit dislocations were observed in the TEM investigations. The observed contrast modulation is related to the composition modulations resulting from the inherent phase separation tendency of the alloy.[7] As a consequence, there are regions in the QWs with preferred formation of Ga–N and In–As bond configurations. Such composition modulation causes a local strain relief, leading to the observed interface roughening.[7,13] On the contrary, the QWs grown at temperatures lower than 390 °C exhibit abrupt interfaces and there are no detectable contrast modulations, in spite of the buildup of epitaxial compressive strain. The composition modulation and the resulting interface roughening are thereby well suppressed by lowering T_s. Besides, in the TEM image of sample B, which was grown under $T_s=375$ °C with varying R_{BEP}, the QWs showed smooth interfaces independent of R_{BEP} (not shown here). The findings from the TEM results support the results obtained from the RHEED pattern during growth. For sample A, a comparatively bright and streaky pattern was observed at temperatures between 350 and 390 °C, whereas a spotty pattern appeared at temperatures higher than 420 °C.[8] On the contrary, the RHEED pattern of sample B remained streaky throughout the growth of the (Ga,In)(N,As) QWs, showing a weak (2×3) reconstruction pattern. These results reveal that solely T_s has a strong impact on the morphological instabilities of the QWs in the ranges of T_s and R_{BEP} used in this study.

Next, we focus on the N incorporation behavior into the QWs. Figures 3(a) and 3(b) show the SIMS depth profiles for samples A and B, respectively, where the ion counts refer to N. The peaks corresponding to the (Ga,In)(N,As) QWs are clearly resolved. For both samples, the deduced total thickness is in good agreement with the expected value calculated from the nominal thickness of the individual layers. In order to analyze the SIMS data, the features of the ion penetration into the materials must be taken into account. At our measurement conditions, the injected Cs^+ atoms are estimated to have a projected range of 5 nm and a longitudinal straggling of 3 nm. Then the N ion counts coming from a (Ga,In)(N,As) QW can be affected as much as 10% by the adjacent deeper lying QW because of the 11 nm barriers separating the QWs.[14] We can hence make a qualitative study of the N incorporation behavior from the SIMS results. As observed in Fig. 3 for both samples, the N ion counts for the first QW of each series are very high (indicated by arrows in Fig. 3). This is probably due to the incorporation of N that occurred during the growth interruptions. In our analysis, we thus consider the QWs which are not marked with an arrow. For each series of QWs, we have averaged the peak heights

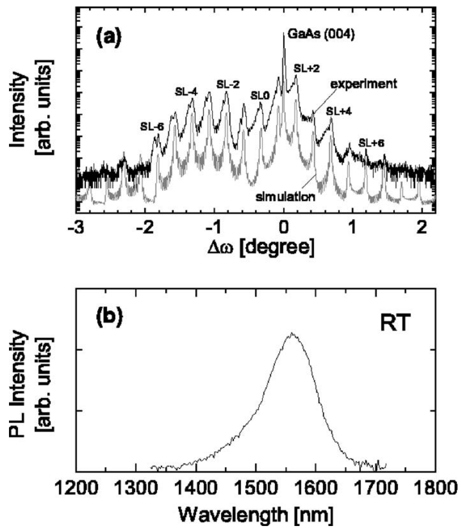

FIG. 4. (a) XRD $\omega-2\theta$ scans and (b) RT PL spectra for the ten-period (Ga,In)(N,As)/Ga(N,As) MQWs, showing emission at 1.56 μm.

after Gaussian fits of the individual peaks. As a matter of clarity, the average values are indicated by parallel bars in Fig. 3. In sample A, the number of ion counts remains nearly the same for each series of QWs, showing almost no dependence on T_s. On the other hand, we observed a strong impact of R_{BEP} on the ion counts of N. In sample B, the ion counts clearly increase with decreasing R_{BEP}. Namely, by reducing R_{BEP}, a higher amount of N is incorporated into the QWs, while T_s has almost no effect on the incorporation behavior. The estimated N concentrations obtained from the analysis of TEM images[7] confirm this result: in sample A, the estimated N content remains nearly constant around 4.6% for T_s between 320 and 450 °C, whereas in sample B, 4.5% N and 3.7% N are incorporated in the QWs grown at $R_{\text{BEP}}=5$ and $R_{\text{BEP}}=50$, respectively. Similar results have been reported by other workers; however, their studies were restricted for the materials of Ga(N,As) or (Ga,In)(N,As) containing less than 1.2% of N, within the higher temperature regime between 400 and 500 °C.[15,16] A possible explanation for the observed N incorporation behavior is that the lower As BEP allows the introduction of larger amounts of N in the layers due to the reduced competition for the incorporation of group V elements.[15] In our case, the reduction of R_{BEP} from 50 to 3 leads to the incorporation of more than 4% N into the QWs, preserving smooth interfaces with no detectable composition modulations.

Finally, we have grown MQWs under the low T_s of 375 °C and low R_{BEP} of 5 to examine the above interpretations. The MQWs consist of ten periods of [(Ga,In)(N,As) (7 nm)/Ga(N,As) (14 nm)], where the QW width was chosen to obtain the desired 1.55 μm emission. Figure 4(a) shows the x-ray diffraction scan for the MQWs. The XRD curve exhibits satellite peaks up to ±6th order with interference fringes, proving the high structural quality of these MQWs.[8] From the theoretical fit assuming coherently strained layer structure, we obtained the composition of 36% In and 4.5% N for the (Ga,In)(N,As) QWs. Figure 4(b) displays the room temperature (RT) PL spectra of this MQWs. Note that rapid thermal annealing at 720 °C for 60 s was employed to enhance the luminescence yield prior to the PL measurements. The observed spectral peak position at 1.56 μm is very close to the desired wavelength of 1.55 μm. The full width at half maximum of this peak is 50 meV, which is similar to that of samples grown using Sb as surfactant.[3] These results verify the feasibility of the low substrate temperature and low As BEP growth concept for the growth of high-quality (Ga,In)(N,As) QWs for long wavelength emission.

In summary, we have investigated the impact of the substrate temperature and As BEP on the molecular beam epitaxial growth of (Ga,In)(N,As) MQWs. The low substrate temperature prevents composition modulations. The low As BEP allows the introduction of large amount of N into the layers due to the reduced competition for the incorporation of group V elements. The low substrate temperature and low As BEP growth concept is found to be a very efficient approach to achieve 1.55 μm emission by allowing the incorporation of large amounts of N without degrading the structural and optical properties.

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