Interplay between the growth temperature, microstructure, and optical properties of GaInNAs quantum wells

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We investigated the influence of the growth temperature (T_{gr}) on the microstructure and on the optical properties of GaInNAs quantum wells (QWs). By comparing the structural information (transmission electron microscopy) with the optical properties (photoluminescence spectroscopy), we demonstrate that high photoluminescence efficiency of GaInNAs QWs is achieved only when the two-dimensional growth mode is preserved, which can be obtained at a low T_{gr} even for high In content. We also show composition modulations in the GaInNAs QWs, which can lead to the interface roughness. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1577393]

Recently, group III–N–As alloys have been intensively investigated due to their intriguing physical properties and promising applications in lasers for telecommunication[1] as well as in high-efficiency solar cells.[2] In fact, the strong band gap reduction upon N incorporation in III–N–As alloys[3] can be theoretically achieved for lattice-matched layers on GaAs substrates using the GaInNAs quaternary alloy.[4] Many works have thus been devoted to this alloy grown as low-dimensional systems.[5–8] However, GaInNAs-based heterostructures exhibit poor optical properties with increasing N content.[9] Moreover, the photoluminescence (PL) is very sensitive to the applied growth temperature (T_{gr}),[10] which seems to be the crucial parameter. Nevertheless, the origin for the strong influence of T_{gr} on PL is still unclear. Finally, there is a lack of knowledge about the real microstructure of the GaInNAs layers and its impact on the optical properties.

In this work, we first investigate the influence of the structural properties on the PL for various GaIn(N)As quantum wells (QWs) confined by Ga(N)As layers. By varying T_{gr}, a clear relation between PL efficiency and growth mode is achieved. Then, we examine and discuss the interplay between the composition modulation in the GaInNAs QWs, the interface roughness, and the strain relief.

The samples were grown by molecular beam epitaxy on (001) GaAs substrates in a Riber system using solid-sources for group-III and As elements and an Addon radio-frequency plasma source precursor for N. The growth runs were controlled by *in situ* reflection high-energy electron diffraction (RHEED).[5] For both the GaInNAs and GaInAs QWs, the thickness was ~7 nm with In and N concentrations in the range of 25%–35% and 2.5%, respectively. The In and N contents were determined using the contrast analysis of (002) dark-field transmission electron microscopy (TEM) images based on the kinematical theory[11] combined with high-resolution TEM techniques[12] carried out in a JEOL 3010 microscope equipped with a GATAN slow scan charge coupled device camera. The cross-sectional specimens were prepared by mechanical polishing followed by Ar^+ ion milling. The optical properties of the as-grown samples were investigated by PL spectroscopy at low temperature (13 K). The PL was excited with the 488 nm line of an Ar laser (excitation density of $\sim 1.5\ \mathrm{W\,cm^{-2}}$) and detected by a cooled Ge detector located at the exit of a 64 cm monochromator.

In the first set of samples S135–S138, T_{gr} was varied between 400 and 475 °C. Each sample contains two QWs, GaInNAs and GaInAs, grown under the same conditions and confined by GaAs barriers. Growing two QWs in one sample offers the advantage of a direct comparison between GaInNAs and GaInAs alloys in terms of the PL efficiency and the strain relief process. Figures 1(a), 1(b), and 1(c) display (110) cross-sectional dark-field images taken with a diffraction vector **g**=002, which is sensitive to the composition of the alloy.[11] Each sample clearly exhibits the two QWs, where the GaInNAs QW is marked with an asterisk for clarity. It is remarkable that the structural quality of the GaInAs QWs does not show any dependence on T_{gr} in the applied temperature range, while the GaInNAs QWs develop interface roughness with an increase of T_{gr}. Indeed, at $T_{gr}=400$ °C, the GaInNAs QW exhibits perfect two-dimensional (2D) features [see sample S137 in Fig. 1(a)]. When T_{gr} is increased to 450 °C, the morphology of the second interface (near to the free surface) becomes rough [S135, Fig. 1(b)] and, finally, at 475 °C the growth results in the formation of an island-like structure [S138, Figs. 1(c) or 2], as expected for a Stranski–Krastanov growth. Furthermore, a perfect correlation between this growth mode transition and the PL intensities is demonstrated. Figures 1(d), 1(e), and 1(f) show the PL spectra measured for samples S137, S135, and S138, respectively. As seen in this figure, the PL efficiency of the GaInNAs QW decreases with increasing T_{gr}. Simultaneously, the contrast modulations related to composition fluctuations in the QW become more pronounced. The GaInNAs QW grown at higher T_{gr} exhibits a low PL intensity due to the three-dimensional growth mode, as confirmed by the spotty RHEED pattern observed during growth.[13] The

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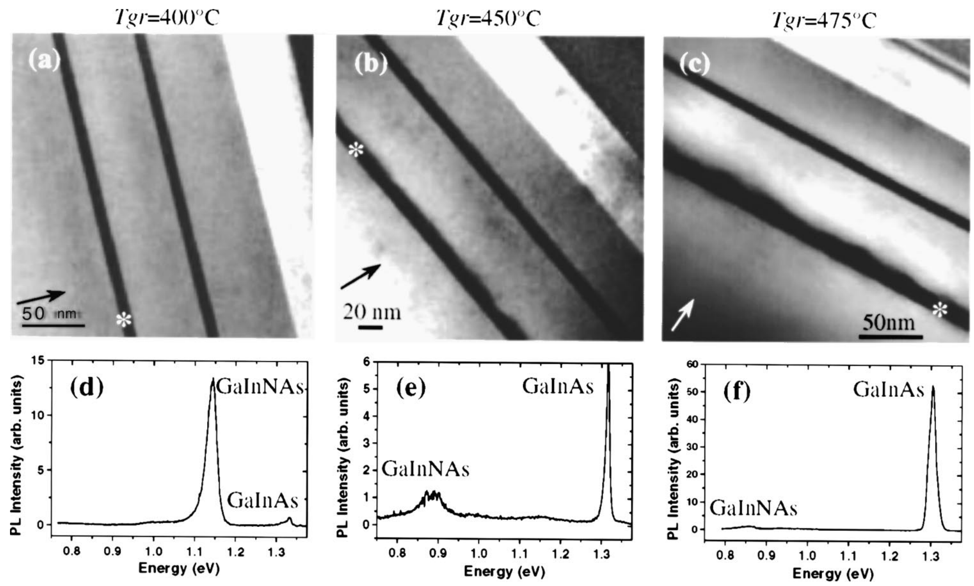

FIG. 1. (110) cross-sectional images taken under dark-field conditions with a diffraction vector **g**=002 for three samples, each of which contains one quantum well of GaInNAs and one of GaInAs: (a) S137 grown at 400 °C, (b) S135 at 450 °C, and (c) S138 at 475 °C. Arrows indicate the direction of **g**, which is also the growth direction. The GaInNAs QWs are identified by the symbol *, the other dark contrasts being the GaInAs QWs. The bright layers near the free surface are the AlGaAs cap layers. The corresponding PL spectra obtained at 13 K from the as-grown samples are given in (d), (e), and (f), respectively.

line broadening which occurs at high T_{gr} could confirm the presence of thickness and composition modulations. In contrast to GaInNAs QWs, the PL efficiency of the GaInAs QWs is significantly degraded when T_{gr} is lowered, the optimum T_{gr} for GaInAs growth being ~510 °C. These results verify that low growth temperatures must be used to prevent surface roughness and island-like behavior of the GaInNAs QWs since the perfect 2D layers provide the best PL efficiency.

We now turn to the origin of the interface roughness in GaInNAs QWs. Generally, the stress in an epilayer can be relieved by a morphological instability coupled with composition inhomogeneities,[14] resulting in an island-like growth. Figure 2 represents a (110) cross-sectional dark-field image of sample S138, taken with a diffraction vector **g**=004. Under this diffraction condition, the observed contrast is based on surface strain distributions. The strain contrast is clearly consistent with the long-range composition modulations verified in Fig. 1(c). Furthermore, a periodicity of about 50 nm is observed along the QW (see arrows). Such a periodicity could be the result of strain due to the lattice mismatch $\epsilon=(a^{GaInNAs}-a^{GaAs})/a^{GaAs}$ between the GaInNAs layer and the GaAs substrate. In the following, this strain is called epitaxial or "external strain." A comparison with the morphology of the GaInAs QWs grown under the same conditions allows a first assertion. The GaInAs QWs exhibit sharp interfaces without any modulations in the whole range of T_{gr} investigated in this study [cf. Figs. 1(a)–1(c)]. Moreover, no oscillation is observed in Fig. 2 in the InGaAs QW in spite of the larger lattice mismatch: 1.4% for the GaInAs QW compared to 1.1% for the GaInNAs QW. Therefore, the external strain is not a complete explanation for the structural morphology of the GaInNAs QW. As both Ga and N atomic radii are smaller than In and As, respectively, the origin of the roughness is then more driven by a "local strain" derived from the atomic size and ionicity differences of the alloy constituents. As demonstrated by Glas,[15] such atomic-size differences are, in fact, a source of morphological-compositional instabilities. The critical temperature for inducing these instabilities is found to be lower for GaInNAs than for GaInAs because GaInNAs alloys are unstable due to the extremely low equilibrium solubility of N in GaAs or GaInAs.[16]

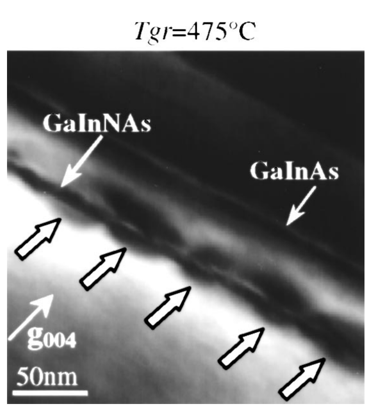

FIG. 2. (110) cross-sectional dark-field image taken from sample S138. The diffraction vector used is **g**=004, sensitive to strain. The pseudoperiodic contrast marked by the wide arrows is due to a periodicity in the local strain, related to composition fluctuations.

In order to clarify the assertion given earlier, one GaInNAs QW confined by GaAsN barriers was grown (sample S221). The In composition in the GaInNAs was increased to ~32% while the N content was kept constant at ~2.5% in both GaAsN and GaInNAs layers. Figure 3 shows the cross-sectional TEM image of the whole structure in (002) dark-field mode. It should be noted that even at higher In content, the GaInNAs layer remains 2D by using the low T_{gr} of 410 °C. The two thin dark lines observed in the figure correspond to the interfaces of the GaInNAs QW, indicating gradual profiles of composition.[17] The GaAsN barrier layers are clearly seen with a darker contrast compared to the GaAs matrix while the GaInNAs QW has just a slightly reduced intensity as expected from the (002) kinematical theory.[18]

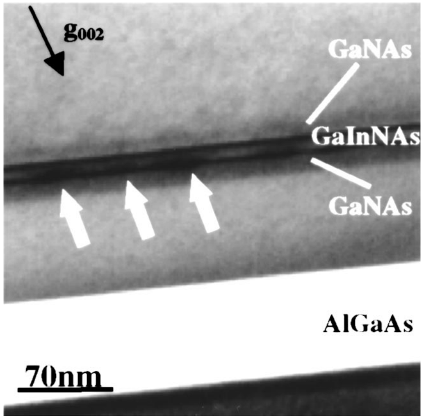

FIG. 3. (110) cross-sectional dark-field image for the sample S221 containing one GaInNAs quantum well confined by GaAsN barriers taken with a diffraction vector **g**=002, sensitive to composition.

The two GaAsN layers exhibit no composition fluctuation, whereas a composition modulation can be detected in the GaInNAs QW. It is interesting to note that the modulation does not appear at the first interface but it evolves during the growth of the QW. So, this represents the initial step of the process that we have already described earlier when discussing Figs. 1 and 2. Moreover, the same periodicity of about 50 nm is measured even though the mismatch of about 1.9% of the GaInNAs QW in S221 is quite different. The wavelength of the roughness periodicity is, thus, initiated by a periodic composition modulation and is not directly related to ϵ of GaInNAs layers in contrast to conventional III–V alloys.[19] This confirms that the structural morphology of the GaInNAs QW is not just the result of the external strain. In addition, the periodic contrast may be caused by fluctuations of the In or N mole fractions. Absolute fluctuations of $\sim\pm1\%$ In the chemical composition of the GaInNAs QW are sufficient to induce the measured contrast variations, while variations of $\sim 2\%$ N would be needed due to a lower sensitivity of the 002 dark-field intensities to N variations in this range of composition.[18] Therefore, we can conclude that the lateral modulations detected in Fig. 3 are, more easily related to variations of the In mole fraction. In addition, the atomic-scale surface roughness during growth can also favor the alloy decomposition. In fact, the atoms of the binary system, which is the most strained by the substrate, segregate towards the upper area.[20] The observed modulations in conventional TEM can be, thus, more related to InAs-rich areas. The roughness is, in turn, enhanced by the decomposition process. It should be noted that this behavior was not observed in InGaAs QWs grown under the same conditions. This means that the presence of N, even in small amounts, induces the particular behaviors of these alloys. However, although composition modulations are not detected in the GaAsN ternary alloy, we cannot exclude N fluctuation in the quantum well with this simple technique.

In summary, we have clearly shown the correlations between the growth temperature, the microstructural, and the optical properties of GaInNAs QWs. The PL intensity is strongly related to the structural quality of the QW. The best results are obtained with 2D grown QWs, which are achieved by using a low growth temperature. The critical parameter for the structural quality of the QW is not the 'external strain' due to the lattice mismatch but the "internal strain" due to the presence of atoms with huge differences of atomic sizes and ionicity, leading to a composition modulation even in the 2D QWs. The composition modulation is a step towards interface roughness.

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