Structural and Optical Properties of III-III-V-N Type Alloy Films and Their Quantum Wells

（ III-III-V-N型混晶薄膜および量子井戸の構造的および光学的性質）

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Abstract

This thesis presents a systematic study of the structural and optical properties of III-III-V-N type alloy films and their quantum wells (QWs), with special emphasis on (i) the influence of N incorporation on physical parameters such as the band-gap value (E_g), lattice constant and strain state, (ii) the physical mechanism of photoluminescence (PL) and photoreflectance (PR) and (iii) the micro-structural and compositional characterizations. In addition, the growth of this type quaternary alloy using metalorganic vapor phase epitaxy (MOVPE) by employing dimethylhydrazine (DMHy) as the source of N has been also investigated.

First of all, the MOVPE growth of $In_xGa_{1-x}As_{1-y}N_y$ alloy films and relevant QW structures are described. Trimethylgallium (TMG), trimethylindium (TMI), AsH_3 and dimethylhydrazine (DMHy) were used as the source materials. After the growth of a 0.3 μm-thick GaAs buffer layer at 700 °C, an InGaAsN layer with the thickness of 200-500 nm was deposited at 530 and 600 °C. The SQWs and MQWs with GaAs barriers and $In_xGa_{1-x}As_{1-y}N_y$ wells were grown on GaAs (001) substrates using the same growth conditions of the thicker epilayers. The layers with various N concentrations were obtained by changing the molar flow ratio of DMHy to the total group V elements. Alloy compositions (x, y) were estimated by high resolution X-ray diffraction (HRXRD) mapping and secondary ion mass spectroscopy (SIMS) measurements. No evidence was found of any influence of the presence of N on the In incorporation for low In contents ($x \sim 11.6\%$ and 13.5%). In this case, the N concentration up to 3.1% has been realized in InGaAsN alloy layers. This is the highest value of N in both GaAsN and InGaAsN materials grown by MOVPE. On the other hand, for the higher In content of x ~ 30%, the In incorporation was remarkably influenced by the present of N in InGaAsN. It is found that In content increased from $x = 27.7$ % (InGaAs) to $x = 31.1$ % (InGaAsN) when the N content increased from $y = 0$ to $y = 1.5$ %.

Then, the structural properties of the MOVPE grown $In_xGa_{1-x}As_{1-y}N_y$ alloy films and their QWs have been evaluated, focusing especially on the evolution of strain state and the generation of structural defects owing to the incorporation of N. It is clear that the compressive strain is strongly reduced with incorporating N into ternary InGaAs. TEM analysis demonstrated the reduction of misfit dislocations in the InGaAsN alloy layers with

increasing N content. On the other hand, in the case of higher In contents ($x \sim 30\%$), a lot of threading dislocations was observed due to a large lattice-mismatch between layer and the substrate ($\varepsilon_o \sim 2\%$). Further investigation shows that the incorporation of N into InGaAs strongly affects the local bonding of N atoms by changing the local strain distributions, resulting in the formation of significant fraction of In-N bonds.

An intensive study on PR in $In_xGa_{1-x}As_{1-y}N_y$ alloy films is presented. The alloy films with different compositions corresponding to the RT-PR signal (E_o transition) wavelength range of 0.98-1.36 μm (0.91-1.26 eV), were grown. The temperature dependence of the fundamental band-gap transition, E_o, have been determined and numerically analyzed. The temperature induced shift of the band-gap energy in InGaAsN was substantially reduced by the presence of N in InGaAs. It is found that the redshift of the band-gap energy in InGaAsN for the temperature increase from 0 K to 300 K was reduced to about 70 % of that of InGaAs. As the N content increases, the broadening parameter Γ of the PR spectra becomes larger compared to the value of Γ obtained with InGaAs. This implies that the broadening parameter Γ is related to the presence of extended defects in the InGaAsN layers associated with the presence of N.

The luminescence property of the $In_xGa_{1-x}As_{1-y}N_y$ alloy films has been systematically investigated. For $x = 11.6$ % and 13.5 % and $y \leq 2.2$ %, at low temperatures ($T < 100$ K), the PL spectra are dominated by multiple peak emissions which involve both near-band-edge emission (high energy peak (E_{PH}) and lower energy peak (E_{PL})) and one associated with the strongly localized state (lowest energy peak, E_x) much lower than the InGaAsN band-gap (E_o transition). With further increase in temperature ($T \geq 100$ K), the PL spectra are excellent with a single near-band-edge emission peak corresponding to their own E_o transition. On the other hand, for higher In ($x \sim 30$ %) and higher N ($y > 2.2$ %) contents, a very broad PL peak was observed and attributed to the emissions from the In-, N-rich quantum-dot-like regions formed with the composition fluctuations.

The energy difference of E_{PH} and E_{PL} peaks is in good agreement with the activation energies (E_{a1}) of the localized excitons/carriers, as confirmed by the theoretical fits. The dissociation energies (E_{a2}) of free-exciton was estimated to be about 18 - 36 meV, which increases with increasing N concentration. The α values extracted from the relation $I_{PL} \propto I^{\alpha}_{exc}$ were used to examine the recombination process. In the N-containing layers it is demonstrated that free-excitons, not free-carriers, mainly govern the radiative recombination. This result is consistent with the results of temperature-dependent PL that the radiative recombination process is strongly modified with a significant number of excitons generated in the InGaAsN alloy layers.

A systematic investigation of the effect of rapid thermal annealing (RTA) on the optical properties of InGaAsN epilayers has been also presented. Three effects are suggested to account for the observed dramatic improvement in the quality of the $In_xGa_{1-x}As_{1-y}N_y$ alloy layers and the $In_xGa_{1-x}As_{1-y}N_y$/GaAs QWs after RTA: (i) improved composition uniformity of the $In_xGa_{1-x}As_{1-y}N_y$ alloy, deduced from the PL, PR and HRXRD measurements, (ii) significant reduction in deep-defects, revealed by low-temperature PL and temperature dependent PL measurements, and finally (iii) significant decrease in nonradiative recombination centers, which results in the strong RTA-induced increase in PL efficiency observed up to room temperature. The PL peak energy position, which was observed in the defect-free layers (low In contents of 11.6% and 13.5%), significantly blueshift in energy after RTA. This blueshift of PL spectra is related to the band-edge emission and explained by the homogenization of the initial nitrogen composition fluctuations in the as-grown InGaAsN alloy. On the other hand, the PL peak energy position, which obtained from the layers (high In contents of ~30%) with high density of extended defects, showed a strong redshift in energy after RTA. Based on the energy dispersive X-ray (EDX) analysis, such an RTA-induced redshift in PL peak energy is related to the strong localization emission and explained by the enlargement of quantum dot-like regions formed by the composition fluctuation regions.

Optical properties of the dilute nitrogen $In_{0.116}Ga_{0.884}As_{0.969}N_{0.031}$/GaAs QWs grown by MOVPE have been investigated by using PL and PR spectroscopy. It is clear that the quantum confinement of the carriers to the well manifests itself in both PL and PR for all the InGaAs(N)/GaAs QWs. The PL intensity of the $In_{0.116}Ga_{0.884}As_{0.969}N_{0.031}$/GaAs QWs is larger than that of both the $In_{0.116}Ga_{0.884}As$/GaAs MQW and the $In_{0.116}Ga_{0.884}As_{0.969}N_{0.031}$ bulk epilayer because of the efficient carrier confinement to the well layer due to the large conduction band offset ΔE_c. For the "nitrogenated" QWs, a low energy shoulder possibly induced by the alloy fluctuation can be seen in the low-temperature PL spectra, and the large degree of improvement after RTA implies the existence of a large number of defects acting as nonradiative recombination centers. As the RTA proceeds, the nitrogen composition fluctuations inside the InGaAsN well layer would be homogenized and then decrease the depth of the potential fluctuations. By comparing the experimental results between the before and after annealing InGaAsN/GaAs QWs, the carriers/excitons localization is reduced, and the nonradiative recombination process becomes less serious, indicating that postgrowth annealing is beneficial to the structural and optical quality improvement.

It is also found that the $In_{0.116}Ga_{0.884}As_{0.969}N_{0.031}$/GaAs QWs show a behavior characterized by the two activation energies (ΔE_1 and ΔE_2). The near-band-edge PL in the as-grown $In_{0.116}Ga_{0.884}As_{0.969}N_{0.031}$/GaAs QWs exhibited the activation energies of ~ 5 - 10 meV ($\Delta E_1^{as\text{-}grown}$) and 18 - 30 meV ($\Delta E_2^{as\text{-}grown}$), indicating the defect-related optical transitions. On the other hand, for the annealed $In_{0.116}Ga_{0.884}As_{0.969}N_{0.031}$/GaAs QWs, ΔE_1^{RTA} was found to be in the range 21 - 32 meV, which is very close to the values of $\Delta E_2^{as\text{-}grown}$ for the as-grown samples. It is surprising that ΔE_2^{RTA} (~ 100 - 120 meV) is possibly coming from the energy difference between the transitions of $n = 1$ and $n = 2$ quantum levels.

Finally, both structural and optical properties of $In_{0.176}Ga_{0.824}P_{1-y}N_y$ alloy films ($0 \leq y \leq 8.7\%$) grown on GaP (001) substrates by MOVPE have been investigated. The experimental results are the evidence of high quality films with high N contents up to 8.7%, which is much higher value ever reported for the quaternary III-III-V-N alloy systems. With the incorporation of N, reduction of compressive strain and a strong red shift in both the PL peak energy and the absorption edge of PL excitation (PLE) were clearly observed. The residual strain sufficiently relaxes for the films with low N contents ($0\% \leq y < 3.4\%$). Whereas, for higher N contents ($3.4\% < y \leq 8.7\%$), the InGaPN layers were coherently strained on the GaP (001) substrates. The lattice-matched $In_{0.176}Ga_{0.824}P_{0.926}N_{0.074}$ film corresponding to a 10K absorption wavelength of 610.8 nm (2.03 eV) has been obtained. The dominant luminescence mechanism in all the investigated InGaPN layers at low-temperatures is the recombination of excitons trapped by the potential fluctuations of the band-edge.