Nitride-rich $GaN_{1-x}P_x$ growth by photo-assisted metalorganic chemical vapor deposition and its optical characterization

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Mixed group-V nitride semiconductors, such as $GaN_{1-x}P_x$ and GaNAs, are new very attractive materials for light-emitting devices in the range from ultraviolet to infrared wavelength due to gigantic bandgap bowing compared with the other III-V compound semiconductors. It has recently been reported that N-rich hexagonal $GaN_{1-x}P_x$ could be grown on a sapphire substrate by gas-source molecular-beam epitaxy and metalorganic chemical vapor deposition (MOCVD). However, there have been very few reports concerning the optical property of N-rich $GaN_{1-x}P_x$, except for the $GaN_{1-x}P_x$ band-edge emission of photoluminescence (PL). That is, visible PL emission based on the band edge of $GaN_{1-x}P_x$ has not yet been reported at room temperature. That is, the crystal quality of $GaN_{1-x}P_x$ was poor, since $GaN_{1-x}P_x$ has a very large miscibility gap, and it was very difficult to grow N-rich $GaN_{1-x}P_x$.

We carried out the growth of $GaN_{1-x}P_x$ using laser-assisted metalorganic chemical vapor deposition (LA-MOCVD) in order to obtain a N-rich $GaN_{1-x}P_x$ with a larger composition ratio (x) and its visible light emission of PL. That is, laser irradiation during growth is effective for the decomposition of source gases at lower temperatures. An ArF (193nm) laser was used for $GaN_{1-x}P_x$ growth, as shown in Figure 1. The laser power was 0.1W. Trimethylgallium (TMG), ammonia (NH_3), and tertialbuthylphosphine (TBP) were used for source gases. In this method, source gases such as TMG, TBP, and ammonia are expected to be decomposed at lower temperatures. We carried out $GaN_{1-x}P_x$ growth at a temperature lower than 1273K, although GaN is generally grown above 1273K using MOCVD. A pulsed ArF laser was irradiated onto the substrate surface through a viewing port of the MOCVD apparatus during $GaN_{1-x}P_x$ growth. Source gases were introduced on the top surface of the substrate and decomposed on the substrate surface. Sapphire substrates were used for the growth of $GaN_{1-x}P_x$ was different growth temperatures. That is, the growth temperatures were 1273K ~ 1123K. Furthermore, the grown samples were also annealed at different temperatures.

As a result, N-rich $GaN_{1-x}P_x$ was grown at 1073K ~ 1223K. The surface morphologies of $GaN_{1-x}P_x$ were inclined to be improved above 1173K. That is, below 1173K, the $GaN_{1-x}P_x$ growth was island-like, resulting in a roughening of the surface morphology. Using an analysis of secondary ion mass spectrometry (SIMS), we confirmed that P incorporation was about 2% into $GaN_{1-x}P_x$.

Figure 2 shows the photoluminescence spectra of $GaN_{1-x}P_x$ at 77K. In the case of a growth temperature of 1123K and an annealing temperature of 1273K, the PL spectrum of $GaN_{1-x}P_x$ was mainly that of a Mg-doped $GaN_{1-x}P_x$ substrate, since $GaN_{1-x}P_x$ grew as islands. The broad and weak PL spectrum of $GaN_{1-x}P_x$ mainly appeared at a growth temperature of 1173K and an annealing temperature of 1273K, since the surface morphology of $GaN_{1-x}P_x$ was comparatively smooth at a growth temperature of 1173K, resulting in covering the whole surface of the substrate. Furthermore, the $GaN_{1-x}P_x$ PL intensity became stronger by increasing the annealing temperature. That is, the peak-shift of $GaN_{1-x}P_x$ band edge emission from that of $GaN_{1-x}P_x$ was the largest under the condition of a growth temperature of 1173K and an annealing temperature of 1323K after growth. It was observed that the peak shift of $GaN_{1-x}P_x$ band edge emission was over 100meV compared with that of GaN.

The value of this $GaN_{1-x}P_x$ peak shift was larger compared with previously reported values when grown by MOCVD. We also observed the PL spectra of $GaN_{1-x}P_x$ at room temperature, although the peak intensity was weak compared with that measured at 77K. Therefore, LA-MOCVD is very effective for the N-rich $GaN_{1-x}P_x$ growth. It was confirmed that $GaN_{1-x}P_x$ is a promising material for a blue-violet LED on behalf of InGaN.

Acknowledgments

This work was supported by NEDO/JRCM's "The light for the 21' Century" Japanese national project.

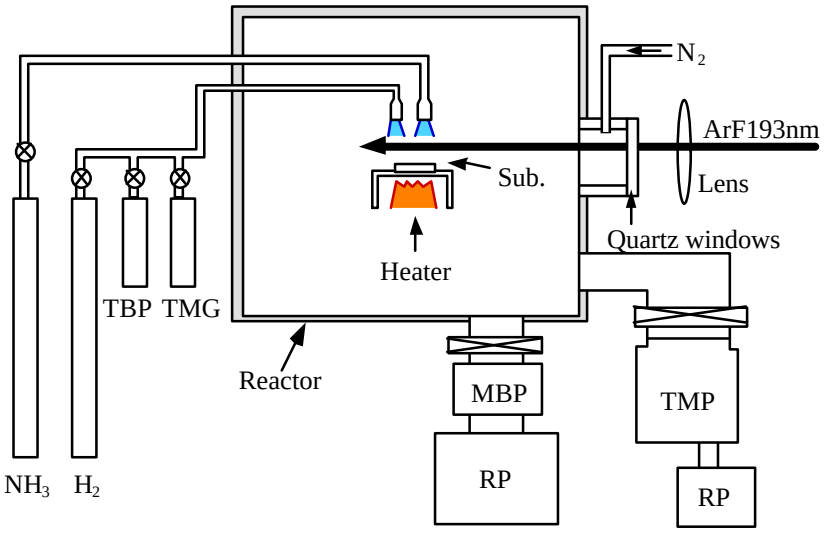

Figure 1 Schematic drawing of a laser assisted MOCVD apparatus

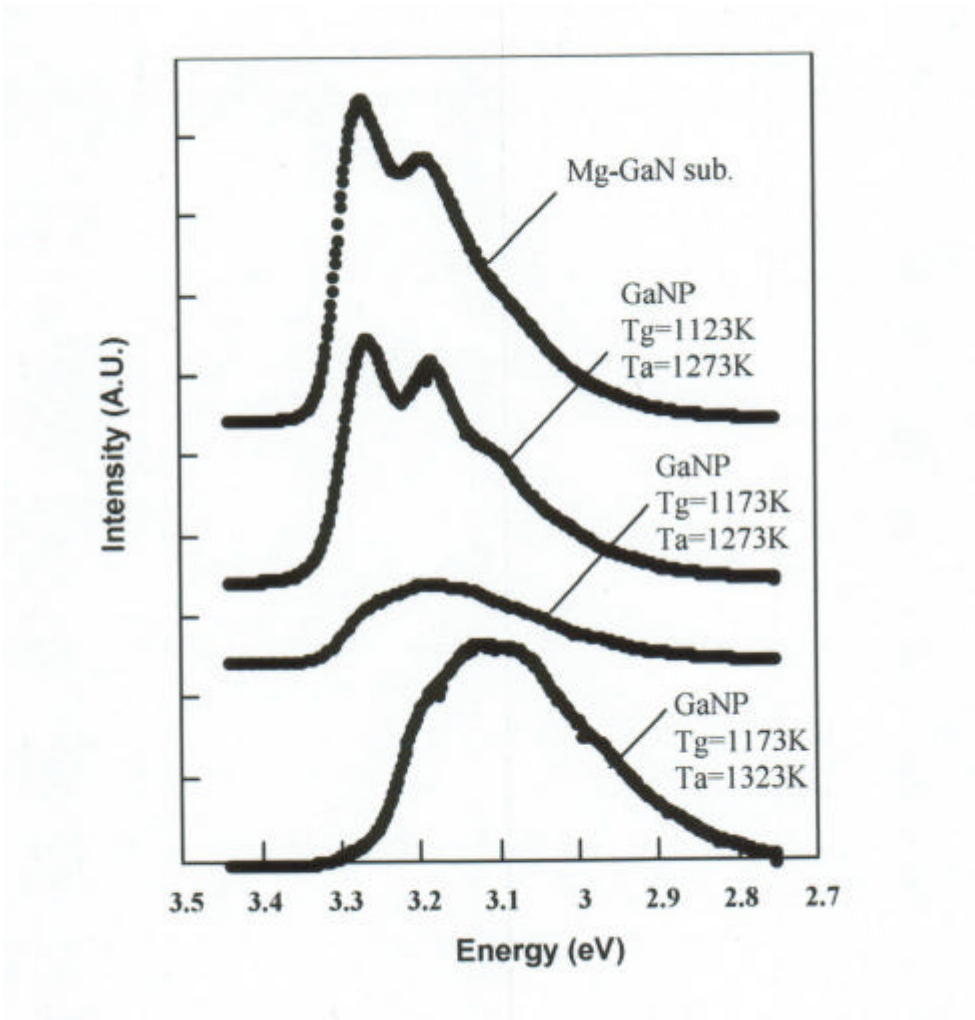

Figure 2 PL spectra at 77K of $GaN_{1-x}P_x$ grown at different growth conditions