Structural and optical properties of AlInN and AlGaInN on GaN grown by metalorganic vapor phase epitaxy

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Abstract

We studied structural and optical properties of Al$_{1-x}$In$_x$N and Al$_{1-x-y}$Ga$_x$In$_y$N films. The films were grown on GaN by atmospheric pressure metalorganic vapor-phase epitaxy. GaN was grown on a c-plane sapphire substrate with a low-temperature-deposited AlN buffer layer. Photoluminescence (PL), absorption and X-ray diffraction measurements of Al$_{1-x}$In$_x$N showed that PL and absorption spectral peaks shift to lower photon energy with increasing alloy composition $x$ and that Al$_{0.83}$In$_{0.17}$N has the highest crystallinity.

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1. Introduction

Much attention has been paid to nitride semiconductors consisting of binaries such as GaN, AlN and InN, in terms of exploring the field of short-wavelength optical devices. In particular, their ternaries, Ga$_{1-y}$In$_y$N and Al$_{1-z}$Ga$_z$N, have been extensively studied and found to be useful as well layers and cladding layers in quantum well (QW) laser diode (LD) structures, respectively [1–3]. In contrast, little attention has been paid to Al$_{1-x}$In$_x$N because of difficulty in its growth from the thermodynamic viewpoint. The difficulty is mainly caused by thermal instability resulting from, for example, the spinodal phase separation phenomenon, which is, in principle more prominent in Al$_{1-x}$In$_x$N than in Ga$_{1-y}$In$_y$N [4]. This effect leads to difficulty in solubility between AlN and InN.

Al$_{1-x}$In$_x$N, however, is very attractive and useful: Al$_{0.83}$In$_{0.17}$N can be lattice-matched to GaN; consequently, Al$_{1-x}$In$_x$N can be used as a cladding layer with no strain on the LD structure, leading to reduction of defects. In addition, Al$_{1-x}$In$_x$N can be adopted as active layer for light-emitting devices in the spectral region from ultraviolet to...
red. Quaternary \( \text{Al}_{1-x-y-z} \text{Ga}_x \text{In}_y \text{N} \) alloys are expected to have similar optical features.

In this paper we present the investigation of structural and optical properties of ternary \( \text{Al}_{1-x} \text{In}_x \text{N} \) and quaternary \( \text{Al}_{1-x-y-z} \text{Ga}_x \text{In}_y \text{N} \) alloys grown on GaN by atmospheric pressure metal-organic vapor-phase epitaxy (MOVPE). GaN was grown on a \( c \)-plane sapphire substrate with a low-temperature-deposited AlN buffer layer. The thickness of the \( \text{Al}_{1-x} \text{In}_x \text{N} \) layers was set to be 1.0 \( \mu \text{m} \), and those of GaN and AlN were 2 and 0.04 \( \mu \text{m} \), respectively.

Structural properties were assessed using triple-axis X-ray diffraction (XRD) measurement. In order to determine the value of composition \( x \), we obtained the \( \omega-2\theta \) scan XRD spectra from the \((0 0 0 2)\) symmetrical plane using an analyzer crystal located immediately before the X-ray detector. Then, we calculated the InN molar fraction \( x \) using Vegard’s law. Energy-dispersive X-ray analysis (EDX) was also performed in order to determine compositions \( y \) and \( z \). For the characterization of the crystalline quality of \( \text{Al}_{1-x} \text{In}_x \text{N} \), we measured XRD spectra from the \((0 0 0 2)\) and \((1 0 1 0)\) planes. In order to measure \((1 0 1 0)\) diffraction, we used the grazing incidence X-ray diffraction method. By measuring the \( \omega \) scan X-ray rocking curves (XRC) from both \((0 0 0 2)\) and \((1 0 1 0)\) planes, two kinds of mosaicity, namely, tilting and twisting, could be characterized independently and directly.

Optical properties were investigated using the optical absorption method, and PL properties, using the He–Cd laser excitation method (325 nm).

2. Result and discussion

Fig. 1 shows the \((0 0 0 2)\) X-ray diffraction (XRD) spectra of \( \text{Al}_{1-x} \text{In}_x \text{N} \) films obtained by the \( \omega-2\theta \) scan. The peak for \( \text{Al}_{1-x} \text{In}_x \text{N} \) is seen to shift to lower angle with increasing alloy composition \( x \), indicating that \( \text{Al}_{1-x} \text{In}_x \text{N} \) films are grown without being affected macroscopically by phase separation and have a wurtzite structure. It is found that alloy composition \( x \) can be varied from 0.01 to 0.58.

In addition, in Fig. 1, the peak for XRD spectrum of \( \text{Al}_{1-x} \text{In}_x \text{N} \) is found to get broader and to show a decrease in intensity with increasing \( x \). This tendency suggests that \( \text{Al}_{1-x} \text{In}_x \text{N} \) is microscopically affected by the phase separation. In fact, as will be shown in Figs. 3 and 4, the spectral linewidth reflects the fluctuation of In concentration, and spectral broadening of PL increases and absorption edge is smeared out in accordance with alloy composition \( x \).

Fig. 2 shows the spectral linewidth of \( \omega-2\theta \) scan of the \((0 0 0 2)\) plane, which represents the distribution of lattice constant \( c \) (\( \Delta c \)). The fact that the value of \( \Delta c \) for \( \text{Al}_{1-x} \text{In}_x \text{N} \) with \( x \leq 0.17 \) remains unchanged (about 700 arcsec) and, for \( x > 0.17 \), \( \Delta c \) increased with increasing \( x \) implies that the \( \text{Al}_{1-x} \text{In}_x \text{N} \) layer for \( x \leq 0.17 \) has a rather small distribution of the lattice constant \( c \). Fig. 2b shows the spectral linewidth of rocking curve scan from \((0 0 0 2)\) diffraction \((\Delta \omega_t)\), which represents tilting. It was revealed that crystalline mosaicity increases with increasing \( x \), indicating that \( \text{Al}_{1-x} \text{In}_x \text{N} \) is grown in unit of grains and that the number of grain boundaries increases accordingly.

The values of \( \Delta \omega_t \) (about 510 arcsec) and \( \Delta \omega_s \) (about 460 arcsec) for \( \text{Al}_{0.83} \text{In}_{0.17} \text{N} \) are the smallest of all values of the \( \text{Al}_{1-x} \text{In}_x \text{N} \) layers examined. Consequently, \( \text{Al}_{0.83} \text{In}_{0.17} \text{N} \), which is
confirmed to be lattice-matched to GaN by reciprocal lattice space mapping, was found to have the highest crystallinity of all the Al$_{1-x}$In$_x$N layers examined in this study.

Fig. 3 shows results of absorption measurement. The ordinate represents $(\alpha)^2$. The absorption coefficient $\alpha$ is related to the band gap $E_g$ by the following relationship: $\alpha \propto \sqrt{E - E_g}$. Extrapolation of the straight lines in Fig. 3 can lead to the band gaps of Al$_{1-x}$In$_x$N. The band gaps are found to shift gradually with varying In content. Tailing of the band gap edge is also found to occur, probably due to fluctuation of In content and due to grain boundaries.

Fig. 4 shows the photoluminescence spectra from Al$_{1-x}$In$_x$N layers that are identical with the ones shown in Fig. 3. The PL peak energy position shifts towards the lower energy region with an increase in In content, similar to that shown in Fig. 3. Considering the fact that PL spectral linewidths are much larger than those obtained assuming a completely random alloy Al$_{1-x}$In$_x$N, mechanisms other than the alloy broadening such as microscopic phase separation contribute to PL peak broadening.

It should be noted that PL spectra in Fig. 4(iii)–Fig. 4(iv) have a component in the infrared spectral region, which implies a lower photon energy than the InN band gap energy (1.89 eV). This implies that Al$_{1-x}$In$_x$N with high In content exhibits an extremely bowing of band gap, and such PL may be due to impurities or point defects. The ratio of PL peak shift (and absorption edge) to that of $x$ is very small. This might reflect the immiscibility of AlN in InN (or vice versa).
Fig. 5. Energy shift of absorption edge and PL peak of Al$_{1-x}$In$_x$N films as a function of In content.

Fig. 5 shows energy shift of absorption edge and PL peak of Al$_{1-x}$In$_x$N as a function of In content. The resulting band gap bowing in this study is very strong, similar to strong bowing which other groups have reported [5–10]. The PL observed in this study is not considered to be result of deep level emission, because the Stokes shift shown in Fig. 5 is not so large, even compared to that of Ga$_{1-x}$In$_x$N and because PL peak energy shifts together with absorption edge energy.

On the other hand, Figs. 6–8 show the $\omega$–$2\theta$ scan XRD spectra and absorption and PL spectra for quaternary Al$_{0.60}$Ga$_{0.38}$In$_{0.02}$N and Al$_{0.21}$Ga$_{0.61}$In$_{0.18}$N films, respectively. The shift in the absorption edge does not agree with that in the PL peak energy. This is probably because of the effect of microscopic potential fluctuations on optical properties.

3. Conclusion

The structural and optical properties of Al$_{1-x}$In$_x$N and Al$_{1-y-z}$Ga$_z$In$_y$N films were
studied. The films were grown on GaN by atmospheric pressure metalorganic vapor-phase epitaxy. GaN was grown on a c-plane sapphire substrate with a low-temperature-deposited AlN buffer layer.

X-ray diffraction measurement (ω−2θ and θ−ω-scans as a function of In content and thickness) showed that Al_{0.83}In_{0.17}N, which is lattice-matched to GaN, has the highest crystallinity. In addition, photoluminescence and absorption measurements showed that each spectral peak shifts to the lower energy region increasing alloy composition x, and that Al_{1−x}In_{x}N system shows strong band gap bowing.

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References