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Estimation of Direct-to-Indirect Crossover of Cubic $Al_xGa_{1-x}N$ Alloy

Atsushi Nakadaira and Hidenao Tanaka
NTT Integrated Information & Energy Systems Laboratories
3-9-11, Midori-cho, Musashino-shi, Tokyo 180, Japan
Phone: +81 422 59 4197, Fax: +81 422 59 2340, E-mail: nakadair@ilab.ntt.co.jp

1. Introduction

Hexagonal group-III nitrides have been extensively studied with the goal of developing devices that take advantage of their wide band-gap energy. Cubic group-III nitrides also have a wide band-gap energy and are being investigated for use in such applications. However, the crystal quality of the cubic nitrides has generally been poorer than that of the hexagonal group-III nitrides. Recently, the crystal quality of cubic GaN grown by metalorganic vapor-phase epitaxy has been improved [1], and the properties of this material have been investigated. Moreover, alloys of cubic group-III nitride are necessary for device applications. We have also reported on the growth and properties of cubic $Al_xGa_{1-x}N$ alloys in the range of $0 \le x \le 0.23$ [2]. Although a cubic $Al_xGa_{1-x}N$ alloy of $0 \le x \le 0.23$ exhibited a direct-gap feature in its photoluminescence (PL), it has been theoretically predicted that cubic AlN has an indirect band-gap energy [3] and that $Al_xGa_{1-x}N$ makes a transition from a direct to an indirect band-gap at about x=0.5 [4,5]. Therefore, it is important to confirm the transition experimentally from the viewpoints of both application and fundamental interest. We report here on the growth of relatively high AlN-composition $Al_xGa_{1-x}N$ alloys and our observation of the indirect band-gap behavior of $Al_xGa_{1-x}N$, which enabled us to estimate the direct-to-indirect crossover.

2. Experiment

We grew $Al_xGa_{1-x}N$ on GaAs (100) substrates using low-pressure metalorganic vapor-phase epitaxy. After cleaning the substrate in an arsenic ambient at 720°C, we deposited a 10-nm-thick GaN layer at 570°C, then a 250-nm-thick GaN layer at 950°C, then finally grew a 500-nm-thick $Al_xGa_{1-x}N$ layer at 950°C. We used trimethylgallium (TMGa), triethylgallium (TEGa), triethylaluminum (TEAl), and NH_3 as source materials. The AlN molar fractions were modified by changing the source flow ratio of TEAl to TEGa. The first and second GaN layers, respectively, prevented the GaAs substrates from roughening and the hexagonal phase from growing in the $Al_xGa_{1-x}N$ layer. Thus, these two GaN layers improved the crystal quality of the cubic $Al_xGa_{1-x}N$ layer. The AlN molar fractions of the films were determined using Auger electron spectroscopy (AES). The highest AlN molar fraction in this report is 0.51. The crystal structure of the films was measured using X-ray diffraction (XRD) in the θ-2θ mode. We measured the optical properties of the films from the PL when excited by the 257-nm emission of a frequency-doubled Ar ion laser.

3. Results and Discussion

Figure 1 shows the XRD pattern of the $Al_{0.41}Ga_{0.59}N$ in the θ-2θ mode. There are three peaks in the range from 30 to 45 degrees, and we believe these peaks originate from the cubic (200) diffraction of the GaAs substrate, GaN, and $Al_xGa_{1-x}N$. These results show that there was a cubic $Al_xGa_{1-x}N$ phase in these films. It was difficult to determine the exact diffraction angles of the peaks from GaN and $Al_xGa_{1-x}N$ in the AlN fraction range of $x \le 0.23$ [2], though, because these two peaks were too close together and too wide. Therefore, it was also difficult to determine the lattice constant. However, it is easier to distinguish between these peaks when the AlN molar fraction is higher since the difference between the peaks be-

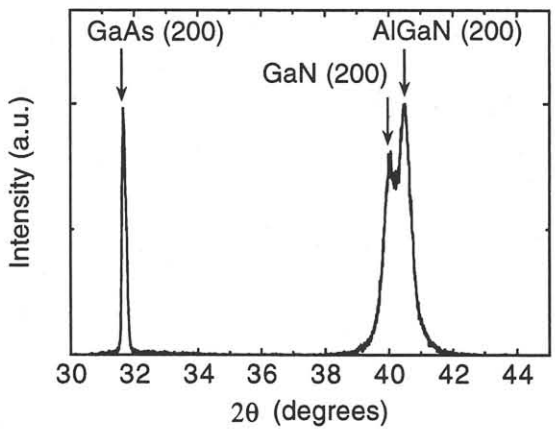

Fig. 1 The θ-2θ mode X-ray diffraction pattern of $Al_{0.41}Ga_{0.59}N$ grown on a GaAs (100) substrate using GaN buffer layers.

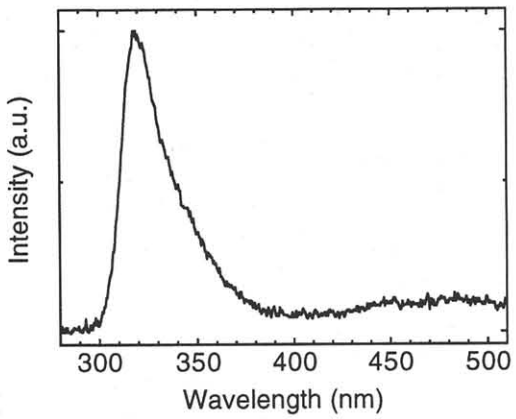

Fig. 2 Photoluminescence spectrum of $Al_{0.41}Ga_{0.59}N$ at room temperature.

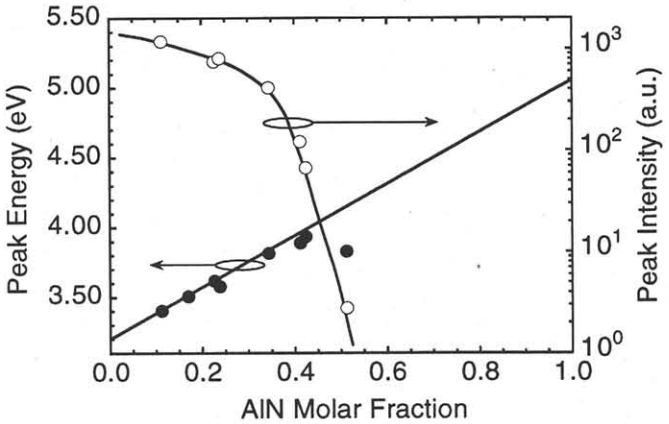

Fig. 3 Near band-edge peak energy and intensity dependence on the AlN molar fraction. The straight solid line shows E=3.20+1.85x.

comes larger. The peaks of GaN and $Al_{0.41}Ga_{0.59}N$ could be assigned at 40.0 and 40.5 degrees. This $Al_{0.41}Ga_{0.59}N$ peak position corresponded to a lattice constant of 4.45 Å. Additionally, the $Al_xGa_{1-x}N$ peak shifted toward a higher angle as x increased. The lattice constants deduced from the angles approximately followed Vegard's rule when we assumed that the cubic AlN lattice constant was 4.37 Å, which was calculated from that of hexagonal AlN.

When we measured the optical properties by PL, the PL spectra showed near band-edge emission even in the range of x>0.23. The PL spectrum of $Al_{0.41}Ga_{0.59}N$ is shown in Fig. 2. The peak energy was 3.89 eV. We could decrease the intensity of the deep-level emission by using TEAl as an aluminum source. Figure 3 shows the peak-energy and intensity dependence on the AlN molar fraction. The peak energy obeys the relationship of E=3.20+1.85x, which was reported in Reference 2, even in the range of $x \leq 0.42$. Therefore, that relationship is applicable in the range of $0 \leq x \leq 0.42$. Since there is no drastic change in the optical properties in this range, $Al_xGa_{1-x}N$ alloys in the range are likely to be direct-gap semiconductors. However, the peak energy of $Al_{0.51}Ga_{0.49}N$ did not follow the relationship and was below that of $Al_{0.42}Ga_{0.58}N$. At the same time, the peak intensity of $Al_{0.51}Ga_{0.49}N$ was one-thirtieth that of $Al_{0.42}Ga_{0.58}N$, and its width suddenly broadened. The red shift of the peak, the sudden intensity decrease of the peak, and the sudden broadening show that $Al_{0.51}Ga_{0.49}N$ has an indirect band gap. It has been theoretically predicted that the direct-to-indirect transition of $Al_xGa_{1-x}N$ occurs around x=0.5 [4,5]. From our results, the direct-to-indirect crossover is in the range of $0.42<x<0.51$, which is consistent with the prediction. The maximum direct-gap energy of $Al_xGa_{1-x}N$ is approximately 3.95 eV. If we assume that the band-gap difference between a clad and an active layer is about 200 meV, we think a-330-nm laser diode can be achieved by using a cubic $Al_xGa_{1-x}N$ alloy system.

4. Conclusions

We grew cubic $Al_xGa_{1-x}N$ on GaAs (100) substrates in the range of $x \leq 0.51$. The XRD peak of high AlN-molar-fraction $Al_xGa_{1-x}N$ could be easily distinguished from that of the buffer GaN layer. The lattice constants estimated from the XRD measurements approximately follow Vegard's rule. The PL measurement showed that $Al_xGa_{1-x}N$ alloys in the range of $0 \leq x \leq 0.42$ have direct gap features and that $Al_{0.51}Ga_{0.49}N$ is an indirect band-gap semiconductor. Consequently, the direct-to-indirect crossover of $Al_xGa_{1-x}N$ appears to occur in the range of $0.42<x<0.51$.

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