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Structural and Optical Properties of $In_xAl_yGa_{1-x-y}N$ Quaternary Alloys

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***Abstract*—**Quaternary $In_xAl_yGa_{1-x-y}N$ semiconductors have attracted much research interest because the use of this quaternary offer the great flexibility in tailoring their band gap profile while maintaining their lattice-matching and structural integrity. The structural and optical properties of $In_xAl_yGa_{1-x-y}N$ alloys grown by molecular beam epitaxy (MBE) is presented. The structural quality of $In_xAl_yGa_{1-x-y}N$ layers was characterized using high-resolution X-ray diffraction (HRXRD). The results confirm that the $In_xAl_yGa_{1-x-y}N$ films had wurtzite structure and without phase separation. As the In composition increases, the Bragg angle of the (0002) $In_xAl_yGa_{1-x-y}N$ peak gradually decreases, indicating the increase in the lattice constant c of the alloys. FWHM of (0002) $In_xAl_yGa_{1-x-y}N$ decreases with increasing In composition from 0 to 0.04, that could indicate the decrease of quality of the samples due to point defects leading to non-uniformity of the epilayers. UV-VIS spectroscopy have been used to study the energy band gap of $In_xAl_yGa_{1-x-y}N$. As the indium (In) compositions increases, the energy band gap decreases. However, for $In_xAl_yGa_{1-x-y}N$ with In composition of 0.1, the band gap shows a sudden increase in energy. This is probably due to local alloy compositional fluctuations in the epilayer. The bowing parameter which appears also to be very sensitive on In content is investigated and obtained b = 50.08 for quaternary $In_xAl_yGa_{1-x-y}N$ alloys. From photoluminescence (PL) measurement, green luminescence (GL) appears at PL spectrum of $In_xAl_yGa_{1-x-y}N$, emitted for all x at ~530 nm and it become more pronounced as the In composition (x) increased, which is believed cause by gallium vacancies and related to isolated native defects.

***Keywords*—**HRXRD, nitrides, PL, quaternary, UV-VIS.

I. Introduction

RECENTLY, III-nitride materials have been extensively studied because of their many applications for optoelectronic devices operating in the range from blue-green to ultraviolet. Quaternary $In_xAl_yGa_{1-x-y}N$ alloys offer increased capabilities for engineering the band gap, lattice constant, strain and polarization of the layers.

$In_xAl_yGa_{1-x-y}N$ alloys have been regarded as the most promising candidates to replace AlGaN or GaN as barriers due to their band gap and lattice constant that could be independently adjusted by varying the indium (In) and aluminum (Al) compositions [1].

Molecular beam epitaxy (MBE) opens up possibilities for the growth of quaternary alloys in the whole composition range, especially for the effective incorporation of In into high-Al-content $In_xAl_yGa_{1-x-y}N$ quaternary alloys [2].

The structural and optical properties of $In_xAl_yGa_{1-x-y}N$ alloys with In mole fraction x ranging from 0 to 0.01 and constant Al mole fraction y = 0.06 grown by MBE is presented.

II. Experiment

The epilayers of $In_xAl_yGa_{1-x-y}N$ alloys were grown on sapphire (0001), with AlN buffer layer using MBE technique. The thickness of the epilayers is between 0.11-0.13 μm as measured by Filmetrics F20-VIS. The structure of the layers was studied by high resolution X-Ray diffraction (HRXRD). The HRXRD were carried out on a PANalytical X'pert Pro MRD with a Cu-$K_{\alpha 1}$ radiation source to evaluate the crystalline quality of the $In_xAl_yGa_{1-x-y}N$ quaternary films. The optical studies were performed in the wavelength range of 300-600 nm by a Hitachi U-2000 Japan double beam spectrophotometer. The absorption coefficient and energy band gap of $In_xAl_yGa_{1-x-y}N$ layers were determined from these measurements. The PL measurements were carried out, by using Horiba Jobin-Yvon HR-800 UV PL system. A He-Cd laser with 325 nm was used as an excitation source. The PL spectra were obtained at room temperature from 330-650 nm.

III. Results and Discussion

The structural properties of the quaternary $In_xAl_yGa_{1-x-y}N$ alloys were analysed by HRXRD. Fig. 1 shows the 2θ XRD spectra of $In_xAl_yGa_{1-x-y}N$ grown by MBE. The XRD measurements confirmed that the heterostructures of quaternary $In_xAl_yGa_{1-x-y}N$ were epitaxially grown on sapphire.

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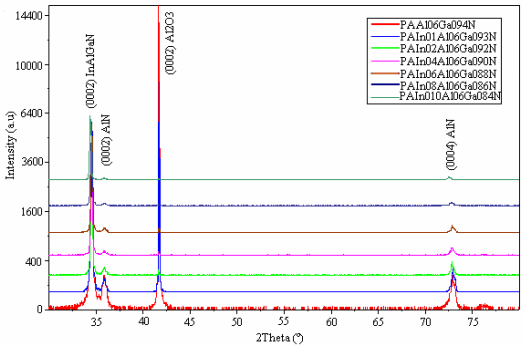

Fig. 1 XRD Phase analysis of $In_xAl_yGa_{1-x-y}N$ quaternary alloys

The pattern revealed (0002) substrate peaks at 41.65°-41.70° which correspond to sapphire (Al_2O_3). The peaks at 34.41°- 34.57° correspond to $In_xAl_yGa_{1-x-y}N$ (0002). The peaks in the range of 35.76°- 35.93° and 72.53°- 72.94° correspond to AlN (0002) and AlN (0004) planes, respectively. These results confirm that the $In_xAl_yGa_{1-x-y}N$ films had wurtzite structure and without any phase separation.

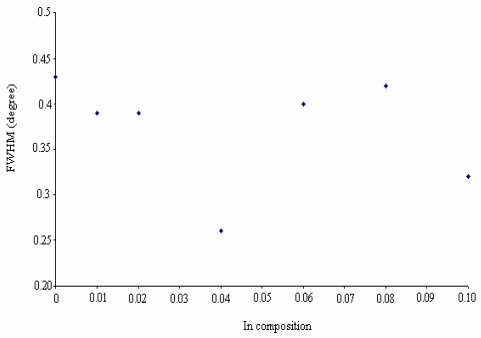

Fig. 2 Full width at half maximum (FWHM) intensity of the (0002) quaternary $In_xAl_yGa_{1-x-y}N$ alloys as a function of the In mole fraction using XRD rocking curve

To investigate the crystalline quality of the epilayers, the XRD rocking curve was also carried out in this study. Fig. 2 represents the full width at half maximum (FWHM) intensity of quaternary $In_xAl_yGa_{1-x-y}N$ alloys (0002) peaks as a function of the In mole fraction using XRD rocking curve. FWHM of (0002) $In_xAl_yGa_{1-x-y}N$ decreases with increasing In composition from 0 to 0.04, that could indicate the increase of quality of the samples. However, for $In_xAl_yGa_{1-x-y}N$ with In composition of 0.06 and 0.10, the figure shows a sudden increase in FWHM. This is probably due to local alloy compositional fluctuations (ACF) in the epilayer, contributed by incomplete substitutions of Ga atoms that introduced point defects leading to non-uniformity of the quaternary alloys [3,4,5].

The optical properties were investigated in the spectral region of 300-600 nm using UV-VIS spectroscopy. Using these data, the absorption coefficient, α can be calculated by applying the relation:

$$\alpha = \frac{2.303}{d}\ln\left(\frac{1}{T}\right) \quad (1)$$

where d and T are, respectively the film thickness and the transmittance.

The composition of the quaternary alloys covered the band gap range from 3.72 eV down to 1.86 eV. The band gap decreases with increasing In composition from 0.01 to 0.08. This trend is expected since the incorporation of In lowers the energy band gap of $In_xAl_yGa_{1-x-y}N$ [6]. However, for $In_xAl_yGa_{1-x-y}N$ with In composition of 0.10, the band gap shows a sudden increase in energy. This is probably due to a more significant effect of the local alloy compositional (ACF) in the epilayer contributed by incomplete substitutions of Ga atoms that introduced point defects leading to non-uniformity of the quaternary alloys.

Fig. 3 shows the variation of the energy band gap of $In_xAl_yGa_{1-x-y}N$ with Al composition of 0.06 and In composition ranging from 0 to 0.10 at room temperature. From the best fit of the non-linear interpolation of the UV-VIS transmission data, the composition dependence of the E_g of the $In_xAl_yGa_{1-x-y}N$ alloys in the composition range of $0 \le x \le 0.08$, for a constant y = 0.06, can be expressed as follows:

$$E_g(In_xAl_yGa_{1-x-y}N) = 50.08x^2 - 24.37x + 3.59 \quad (2)$$

A downward bowing parameter, b = 50.08 have been obtained. This result is comparable with the reported results [7]. The bowing parameter is used to determine the non-linearity interpolation of the energy gap functional dependence on composition and appears also to be very sensitive on In content.

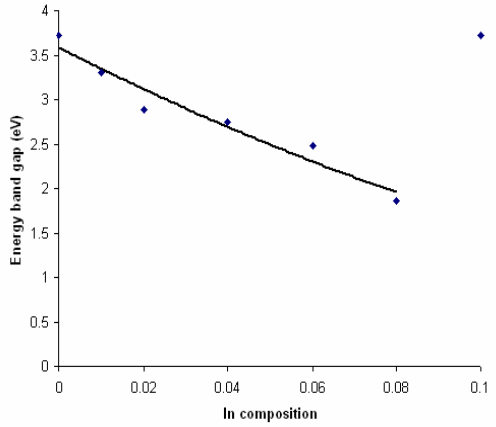

Fig. 3 The energy band gap versus In composition plot of $In_xAl_yGa_{1-x-y}N$

The explanation for the b sensitivity on In-content in quaternary alloys could be the strong volume deformation in alloys varying In-content, due to large In atomic number and much larger In-N bonds compared to the Ga-N and Al-N bonds [7]. It should be noted here that the data of In = 0.10 is not taken into account for the determination of the bowing parameter because its energy band gap is placed outside the trend line of the other data.

Fig. 4 shows the room temperature photoluminescence spectra of the quaternary samples $In_xAl_yGa_{1-x-y}N$ with the

constant Al content (y = 0.06) and different In composition (x varies from 0 to 0.1). The spectra for x = 0 and x = 0.01, there is one dominant peak with narrow FWHM at ~342 nm with energy band gap of 3.63 eV [8]. The presence of several peaks at x = 0.02 and 0.04 indicated point defects which originated from transition of defects energy levels in the band gap. At this point, their dominancy interchanges with different value of x. As In composition (x) increased from 0.06 to 0.10, the first peak became broader and decreased in intensity. Moreover, it is slightly shifted to the higher wavelength (redshifts) indicating a decreased in the energy band gap, E_g from 3.63 eV down to 3.09 eV (~402 nm) [9]. This trend is expected since the incorporation of In lowers the energy band gap of $In_xAl_yGa_{1-x-y}N$ [6].

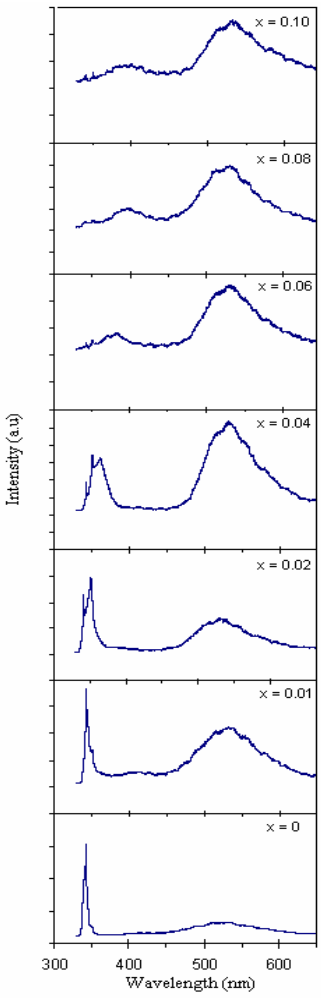

Fig. 4 Room temperature of PL spectra for $In_xAl_yGa_{1-x-y}N$ with constant Al (y = 0.06) and different In composition, x (varied from 0 to 0.1)

From Fig. 4, a secondary broad emission is also observed at ~530 nm. This peak corresponds to the green luminescence (GL) in $In_xAl_yGa_{1-x-y}N$ and most likely cause by gallium vacancies and related to isolated native defect [10]. This GL peak appears at very low intensity for low In mole fractions, but it becomes more pronounces as the In content increased. In principle, this green luminescence actually attributed to the formation of indium-rich cluster. Somehow, the presences of GL at x = 0 is most probably due to the non-uniformity of ternary epilayers [10].

IV. Conclusion

In conclusion, the structural and optical properties of $In_xAl_yGa_{1-x-y}N$ quaternary alloys grown on sapphire by MBE with Al composition of 0.06 and different In mole fraction ranging from 0 to 0.10 has been investigated. The experimental results showed that the $In_xAl_yGa_{1-x-y}N$ epilayers were epitaxially grown on sapphire substrate. XRD rocking curve was used to investigate the FWHM of the (0002) peaks of $In_xAl_yGa_{1-x-y}N$ samples. The band gap of $In_xAl_yGa_{1-x-y}N$ alloys decrease with increasing In composition. However, for In composition of 0.1, the band gap shows a sudden increase in energy. A bowing parameter, b of 50.08 has been obtained through this study. The secondary broad emission is observed through PL measurement, which corresponds to the green luminescence (GL) in $In_xAl_yGa_{1-x-y}N$. These GLs are believed to be related to an isolated native defects (isolated gallium vacancies (V_{Ga}) or isolated complex involving V_{Ga}) in the quaternary alloys.

V. Acknowledgement

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