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Publication IV

S. Suihkonen, O. Svensk, P.T. Törmä, M. Ali, M. Sopanen, H. Lipsanen, M. A. Odnoblyudov and V. E. Bougrov, *MOVPE growth and characterization of InAlGaN films and InGaN/InAlGaN MQW structures*, Journal of Crystal Growth, IN PRESS.

ARTICLE IN PRESS

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Journal of Crystal Growth ■ (■■■■) ■■■–■■■

JOURNAL OF CRYSTAL GROWTH

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MOVPE growth and characterization of InAlGaN films and InGaN/InAlGaN MQW structures

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Abstract

We report on the growth and characterization of InAlGaN films and InGaN/InAlGaN MQW structures by metalorganic vapor phase epitaxy (MOVPE). The composition of the grown films was evaluated by high-resolution X-ray diffraction (HRXRD) and secondary ion mass spectrometry (SIMS) measurements. It was found that increasing the In precursor flow not only increased the In content of the InAlGaN films but also decreased the Al content. Uniform compositional depth profile was achieved when the In content of the films was below 0.02. At higher In contents the InAlGaN/GaN interface became diffused. In the InGaN/InAlGaN MQW samples increasing the In content of the barrier layers to 0.016 was found to cause non-uniform distribution of Al and degrade the optical quality of the samples.

PACS: 73.21.Fg; 78.55.Cr; 78.66.Fd; 78.67.De

Keywords: A3. Metalorganic vapor phase epitaxy; A3. Quantum wells; B1. InAlGaN

1. Introduction

Although blue and green LEDs are commercially available, fabricating efficient ultraviolet (UV) LEDs remains difficult. UV semiconductor light sources are required for a number of applications, including white lighting, sterilization, decontamination and for high-density optical storage [1,2]. For lighting applications, the near UV wavelength range from 350 to 400 nm is especially important, since the UV emission can be converted to white light using efficient phosphors. In order to realize high-power UV emitting LEDs using group-III-nitride materials, it is necessary to obtain high-efficiency emission from wide-band-gap multiple quantum well (MQW) structures. High-emission efficiency can be achieved using MQW structures consisting of InAlGaN barriers and InGaN QWs grown by metalorganic vapor phase epitaxy (MOVPE) [1,3,4]. It has been shown that a small amount of In in the barrier layers significantly enhances the optical properties of the MQW stack [5].

MOVPE growth of quaternary InAlGaN films has proven to be challenging due to the different optimum growth conditions of In and Al containing GaN alloys [6]. Growth of high-quality AlGaN should be performed in H_2 ambient and at temperatures over 1000 °C, while for InGaN growth N_2 ambient and temperatures below 800 °C are needed to enhance In incorporation. The compositional characterization of quaternary InAlGaN films is not a straightforward task. Rutherford back-scattering spectroscopy (RBS), energy dispersive spectroscopy (EDS), secondary ion mass spectrometry (SIMS) and high-resolution X-ray diffraction (HRXRD) have been used for compositional characterization [5,7–10].

In this work we report on our studies on growth and characterization of quaternary $In_xAl_yGa_{1-x-y}N$ layers and

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doi:10.1016/j.jcrysgro.2007.11.122

$InGaN/In_xAl_yGa_{1-x-y}N$ MQW structures. $In_xAl_yGa_{1-x-y}N$ films with x ranging from 0 to 0.05 and y ranging from 0.12 to 0.2 were grown by MOVPE. The composition of the films was evaluated by HRXRD and SIMS. It was found that increasing the In precursor flow caused an increase in x and a decrease in y in the $In_xAl_yGa_{1-x-y}N$ films. An uniform compositional depth profile was achieved, when x was below 0.02. At higher values of x the Al content at the InAlGaN/GaN interface became diffused. In the InGaN/InAlGaN MQW samples sharp interfaces and uniform composition was achieved when the In content of the barrier layers was below 0.01. Increasing the barrier In content to 0.016 was found to cause non-uniform distribution of Al inside the barrier layers and degrade the optical quality of the samples.

2. Experimental procedure

The samples were grown by vertical flow MOVPE on c-plane sapphire substrates covered by 2 μm GaN buffer layer. Trimethylgallium (TMGa), ammonia (NH_3), trimethylindium (TMIn) and trimethylaluminum (TMAl) were used as gallium, nitrogen, indium and aluminum sources, respectively. After the GaN buffer layer growth the temperature was decreased to 850 °C, carrier gas was switched to nitrogen and pressure was increased to 300 torr for growth of the InAlGaN layer. During the growth of the InAlGaN layers TMGa flow of 25 μmol/min, TMAl flow of 51 μmol/min and V/III ratio of 1100 were used. The In composition was varied by changing the TMIn flow in the range of 0–46 μmol/min.

The same growth parameters were used for the InAlGaN barriers in the InGaN/InAlGaN MQW samples. After the growth of each barrier layer the temperature was decreased to 800 °C for the growth of the $In_{0.06}Ga_{0.93}N$ quantum wells.

The crystal quality and layer thicknesses of the InAlGaN layers and MQW structures were characterized by HRXRD (0 0 0 2) $\omega-2\theta$ scans. The composition depth profile was obtained from SIMS measurements. By combining the HRXRD and SIMS measurements it was possible to evaluate the In and Al composition in 10% accuracy. For photoluminescence (PL) measurements 325 nm line of He–Cd laser was used to excite the samples.

3. Results and discussions

Fig. 1 shows the (0 0 0 2) $\omega-2\theta$ scans of InAlGaN films grown on GaN buffers with various TMIn flows. The results show that as the TMIn flow is increased, the InAlGaN XRD peak shifts closer to the GaN peak, and that the InAlGaN layer is almost lattice matched to GaN when a TMIn flow of 46 μmol/min is used. The presence of multiple clear diffraction fringes implicates sharp InAlGaN/GaN interfaces. The full width at half maxima (FWHM) of the InAlGaN peaks varies from 130 to 160 arcsec and is set by the layer thickness. Fig. 2 shows the InAlGaN and GaN peak separation and the growth rate of the InAlGaN films is as a function of the TMIn molar flow. The InAlGaN film thickness was roughly 100 nm in all the samples. It can be seen from Fig. 2 that the growth rate of the film decreases from 0.11 to 0.08 nm/s when the TMIn flow is increased. The XRD peak shift decreases linearly with increasing TMIn flow up to TMIn flow of 21 μmol/min, and saturates slightly at higher flows. This indicates

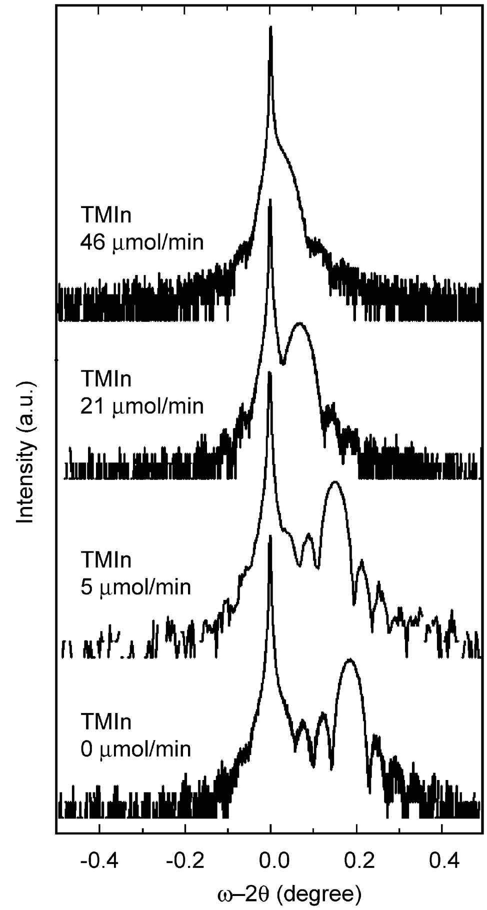

Fig. 1. HRXRD ($\omega-2\theta$) curves of the (0 0 0 2) reflections from InAlGaN films grown with various TMIn flows.

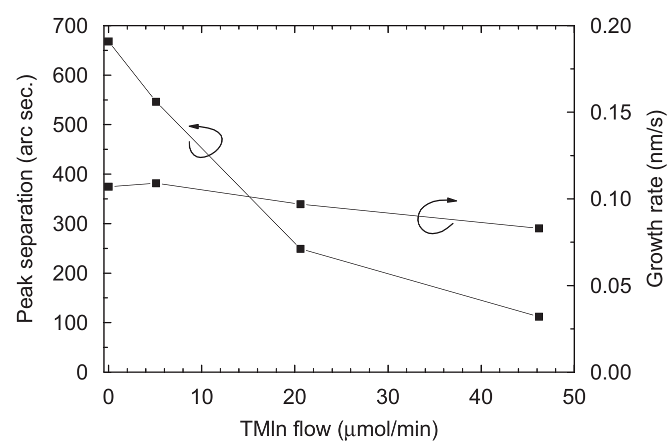

Fig. 2. The InAlGaN and GaN XRD peak separation and growth rate of the InAlGaN films as a function of TMIn molar flow.

that the composition of the film exhibits non-linear dependence on the TMIn flow.

To evaluate the In and Al composition of the films, first the Al content was measured by HRXRD from the sample grown with TMIn flow of 0 μmol/min. This was then used as reference for SIMS measurements. With this method it is possible to evaluate the In and Al contents with 10% accuracy. Fig. 3 shows the In and Al concentrations as a function of TMIn flow. It can be seen from Fig. 3 that the TMIn flow has an effect on both the In and the Al content of the films. The In content of the films increases and Al content decreases with increasing TMIn flow. In the MOVPE growth of InAlGaN films, varying TMAl flow has been reported to affect also the In content [8]. The Al content of the film grown with 46 μmol/min was reduced by 40% compared to the reference sample grown with 0 sccm of TMIn. The decrease of Al content can at least partly result from the reduction of the growth rate of the films. In the MOVPE growth of AlGaN films

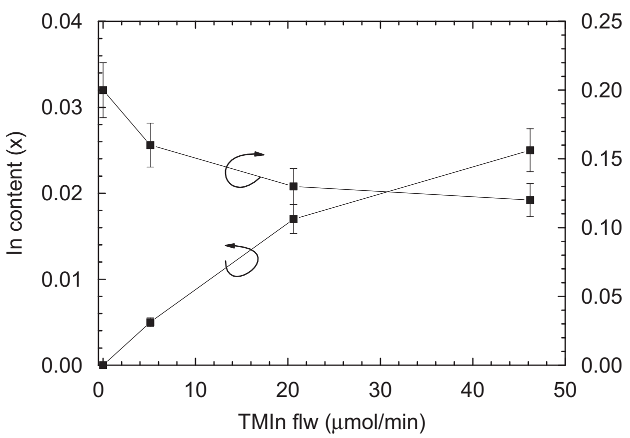

Fig. 3. The In and Al contents of $In_xAl_yGa_{1-x-y}N$ films as a function of TMIn flow.

reducing growth rate has been reported to decrease the Al content [11].

The compositional depth profile of the samples grown with TMIn flow of 21 μmol/min or less shows sharp interfaces and uniform In and Al compositions through out the film. In the sample grown with TMIn flow of 46 μmol/min, the Al content increases gradually from 0 to 0.12 during the first 20 nm starting from the InAlGaN/GaN interface, while the In composition is uniform through the film. This can be seen in the case of MQW structures from Fig. 4b. This cannot result from strain, as the films are nearly lattice matched to GaN (see Fig. 1). The most likely explanation is that the increased In mole fraction disturbs the initial steps of the InAlGaN film growth. This can be due to increased compositional fluctuation of In [10]. As the In fluctuation is in the atomic scale it cannot be seen from the SIMS profile. The exact reasons and mechanisms of this phenomenon are not clear and, therefore further study is needed.

Samples with five-period InGaN/InAlGaN MQW structures were also grown. The InAlGaN barriers of the MQW structures were grown with the same growth parameters as the InAlGaN films described before. The intended QW composition was $In_{0.06}Ga_{0.93}N$ and thickness 2 nm. The composition of the QW and barrier layers were determined by combining the results from SIMS measurements and XRD scans. Fig. 4 shows the SIMS profiles of InGaN/InAlGaN MQW structures with barriers grown using (a) 5 μmol/min (sample A) and (b) 46 μmol/min (sample B) flow of TMIn. The SIMS In composition scans from the both samples show distinct peaks indicating the positions of the five QWs. Clear interference fringes from the MQW stack are also visible in XRD (0 0 0 2) scans, indicating sharp interfaces and uniform layers thicknesses (data not shown).

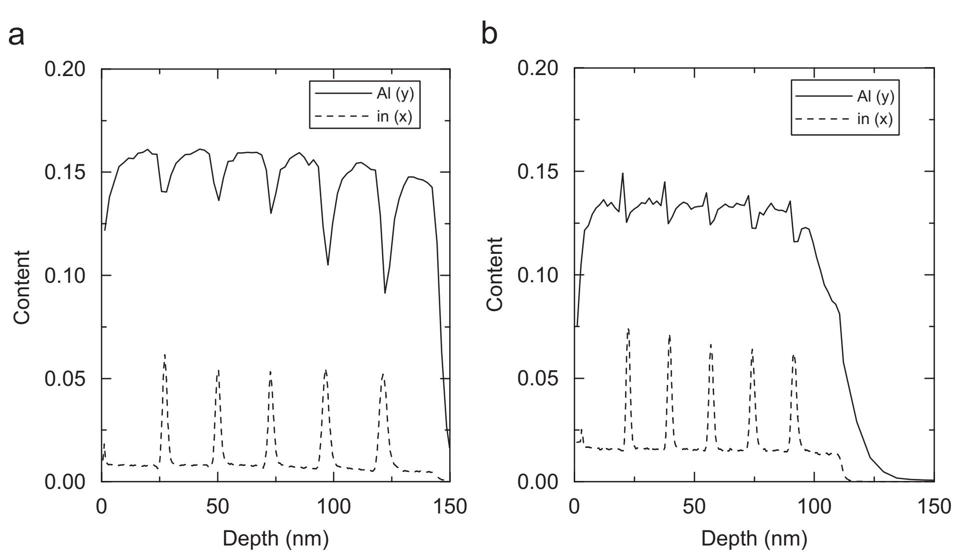

Fig. 4. The In and Al composition depth profiles measured by SIMS of InGaN/$In_xAl_yGa_{1-x-y}N$ MQW samples. TMIn flow of (a) 5 μmol/min (sample A) and (b) 46 μmol/min (sample B) were used during the growth of the InAlGaN barriers.

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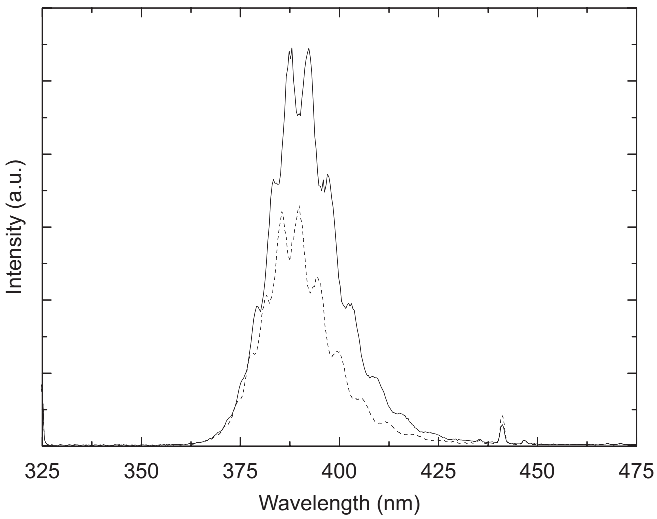

Fig. 5. Room temperature PL spectra of InGaN/InAlGaN MQW samples. Sample A is marked with solid line and sample B with dashed line.

In sample A the barrier thickness is 21 nm and QW thickness 2 nm as measured by XRD. The barrier Al content raises from 0.145 of the first barrier to 0.16 of the topmost barrier, and is fairly uniform inside of a single barrier layer. The In content of the barrier layers is a constant 0.008. In sample B the barrier thickness is only 16 nm and QW thickness 1.7 nm. The Al content of the barriers is 0.13, except for the first barrier, where the Al content increases gradually starting from the InAlGaN/GaN interface at the depth of 110 nm. The tail of Al content below 110 nm comes from the response of SIMS measurements. The In content of the barriers is 0.016. When the barrier compositions are compared with corresponding InAlGaN film compositions, we see that the barriers grown with 5 μmol/min (sample A) have identical In composition compared to the InAlGaN film grown under the same conditions. When the TMIn flow is increased to 46 μmol/min (sample B) the In content of the barrier layers is only 0.016 while the InAlGaN sample grown under these conditions had In content of 0.025. The SIMS profile of the sample B shows also peaks of Al content located on top of the QW layers. We believe that also in the case of MQW structures the high In mole fraction disturbs the growth of InAlGaN barriers. This results in non-uniform distribution of Al inside the barriers and non-stable In incorporation. Also it is likely that the growth and composition of InAlGaN barriers with In content over 0.001 is affected by the underlying layer, as the Al content of the barriers behaves in a different way in InAlGaN/GaN interfaces than in InAlGaN/InGaN interfaces. It can also be noted that the In content of the QWs is higher in sample B than in sample A, this results most probably from the larger amount of In present in the reactor during the growth of the MQW stack.

The optical quality of the samples was determined by room temperature PL measurements. The results are shown in Fig. 5. Both samples have emission maxima at 380 nm and peak FWHM of 18 nm, but the sample A shows 60% higher PL intensity than sample B, indicating better optical quality. The wavelength of the samples is the same, as in sample B red shift caused by the increased In content in QWs is compensated by blue shift caused by the reduced QW thickness.

4. Conclusions

We have investigated the MOVPE growth of InAlGaN films and InGaN/InAlGaN MQW structures on GaN/sapphire substrates. HRXRD and SIMS were used to characterize the composition of the samples. In the case of 100 nm thick InAlGaN films the In content of the films increased and Al content decreased with increasing TMIn flow. The In and Al compositions were found to be uniform up to TMIn flow of 21 μmol/min. With higher TMIn flows the Al content at the InAlGaN/GaN interface became diffused. In the MQW samples sharp interfaces and uniform composition were achieved when the In content of the barrier layers was 0.008. Increasing the In content of the barrier to 0.016 was found to cause non-uniform distribution of Al in the barrier layer and degrade the optical quality of the samples. We believe the non-uniform composition of InAlGaN films and barrier layers results from small-scale fluctuations of the In content that disrupt the initial growth of the InAlGaN layer.

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