Growth of InN and In rich InGaN layers on GaN templates by pulsed MOCVD

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Abstract

InN and In rich InGaN layers have been grown on GaN templates using pulsed MOCVD technique and compared with analogous grown by conventional method. All layers were free of metal droplets. InN showed three times lower background electron concentration $n_e=(8\div9)\times10^{18}$ cm^{-3} and three times higher electron mobility $\mu_e=644$ cm^2/(Vs) than those for conventionally grown material. Morphology investigations demonstrated increase of size (from 100 to 500 nm) and decrease of density of InN islands with growth temperature. For In-rich InGaN layer (80%, 68%) the density of islands was similar to InN, though, the diameter varied from 50 to 150 nm. Structural investigations were performed using XRD and SEM techniques, electrical and optical properties – Hall and photoluminescence. Inhomogeneities of In and Ga distribution in the layers resulting broadened XRD and photoluminescence spectra are discussed.

1. Introduction

Over the past years indium nitride (InN) has become attractive due to discoveries of its inherent optical and electrical properties. Band-gap was found to be about 0.7 eV [1,2]. Continuous change of energy band gap from 0.7 eV for InN to 3.4 eV for gallium nitride (GaN) attracted new applications of InGaN alloys in photovoltaics and terahertz (THz) electronics [3]. Optoelectronics using InN and In rich InGaN have become a topic of interest. Lack of lattice-matched substrates and the superposition of low dissociation temperature of InN (600ºC) with the low degree of ammonia decomposition at such temperatures drives the motivation to develop growth technologies for high quality layers with various In concentration [4-7]. Growth at relatively low temperature results in low decomposition efficiency of ammonia (NH_3) and diffusivity of atoms at crystal surface – main reasons for In droplets formation. In order to get rid of In droplets very high V/III ratio were used providing enough atomic nitrogen, but limiting growth rate and maximizing consumption of nitrogen precursor [8]. *Johnson* and coworkers proposed pulsed growth method for droplet free InN [9]. Still high quality InN layer grown at lower V/III ratio were demonstrated as well [10]. Splendid results of In rich InGaN layer with minimal In segregation using metal-modulated epitaxy was shown by *Moseley* and coworkers [11] where the the pulsed technique was applied to suppress gas phase reaction and also achieved by high-pressure MOCVD [7,12].

In this study, we compared properties of InN layer grown by pulsed and conventional metalorganic chemical vapor deposition (MOCVD) mode. We applied the pulsed technique for growth of In rich InGaN layer.

2. Experimental procedure

InN and In-rich InGaN thin films (100÷200 nm) were grown on GaN/sapphire templates by MOCVD method in a low-pressure 3x2" closed-coupled showerhead reactor. Trimethylgallium (TMGa), trimethylindium (TMIn) and ammonia were used as Ga, In and N sources, respectively. N_2 was used as an ambient and carrier gas. The GaN (0001) templates of 3.5 μm thickness on sapphire were grown using standard low temperature GaN buffer and subsequent high temperature GaN layer growth procedure. InN and InGaN were deposited directly on top of the template without any additional interlayer. All growths were performed at a pressure of 300 mBar and V/III ratio higher than $\sim 2 \cdot 10^4$. The growth temperatures were varied from 580 up to 620°C. In the pulsed growth mode ammonia was constantly flowing, while the TMIn and TMGa were sent into the reactor chamber for 10÷40 s duration pulses, then, bypassed the reactor chamber for 20 s. The reference InN sample was grown by non-pulsed conventional (continuous-flux) growth mode.

X-ray diffraction measurements (XRD, Rigaku, SmartLab) were carried out to investigate the crystalline structure and composition of InGaN layer. The surface morphology of the InN and InGaN layers was investigated by scanning electron microscopy (SEM, CamScan, Apollo 300). Optical properties were investigated by photoluminescence (PL) at room temperature using a continuous wave (cw) laser (λ=633nm) as an excitation source. The PL emission was collected into 0.3 m spectrometer (Andor, Shamrock 303) and detected by InGaAs detector array (Andor, iDus DU491A-2.2). The free carrier density and the mobility in the thin film was determined by Hall-effect measurements in van der Pauw geometry using indium/tin ohmic contacts.

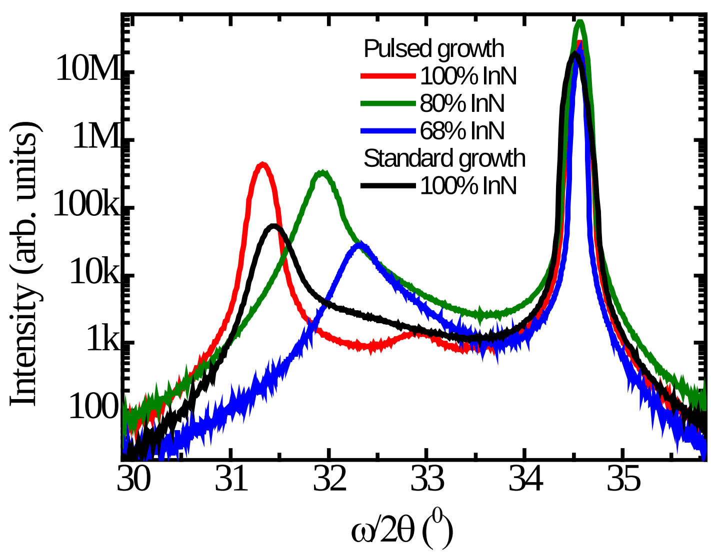

Fig. 1. ω/2θ scans for InN and InGaN layers grown on GaN/sapphire substrates by conventional (black line) and pulsed growth mode (color lines).

3. Results and discussion

High crystalline quality of InN grown by pulsed mode at 600ºC was confirmed by XRD (see Fig. 1). The InN peak in ω/2θ scan was more than 17 times intense compared to the best material grown by conventional mode at 580°C, while the thickness of the layer was similar. High intensities of peaks indicate that the InN layers are of high purity and low crystal lattice distortion in both cases. The decrease of FWHM of ω/2θ scan from 1050 to 820 arcsec indicated better crystalline homogeneity for the layer grown by pulsed mode. The diffraction peak at 31.3°±0.05° of pulsed grown InN (0002) is very close to that expected for unstrained InN (31.33°, grating period c=5.7039 Å) [13]. The slight shift of the peak for sample grown by conventional method originates from lower crystalline quality and incorporation of some impurities like oxygen. The small and wide peak near 33º can be attributed to diffraction from (10-11) of some random InN grains or some In oxide.

Furthermore, an In rich InGaN layer was grown in pulsed mode under the same conditions such us pulse duration, pressure and ammonia flow, as for InN, simply providing additional TMGa flow to the reactor chamber. The In content was estimated from the diffraction peak position (Fig. 1) using Vegard's law and assuming fully relaxed InGaN layer (d ≈ 200 nm). Thus, In concentration in the layer grown at 600°C was 80%, while increase of temperature up to 620°C and increase of TMGa flow lowered incorporation of In down to 68%. Both layers demonstrated rather broad peaks with FWHM 1043 arcsec for 80% and 1436 arscec for 68% indicating presence of InGaN grains with different In, Ga concentration also some crystal grating distortion [14]. No additional peaks were observed.

Better crystal quality of the layers defined better electrical properties, which were measured by Hall effect. InN layer grown by pulsed method showed three times lower background electron concentration and three times higher electron mobility of n_e=(8÷9)×10^{18} cm^{-3} and μ_e=644 cm^2/(Vs), respectively, when compared to conventionally grown InN layer (n_e=2.7×10^{19} cm^{-3}, μ_e=215 cm^2/(Vs)). The values obtained for pulsed grown InGaN with 80% In were accordingly n_e=3.4×10^{19} cm^{-3}, μ_e=141 cm^2/(Vs).

The lattice mismatch between InN (a=3.545 Å) and GaN (a=3.186 Å) is about 10%. Such difference induces compressive strain which leads to elastic relaxation via three-dimensional growth in thin InN layer (Stranski–Krastanov (SK) growth mode) [15]. The critical thickness for the island formation depends on the In concentration and limits the thickness of the two-

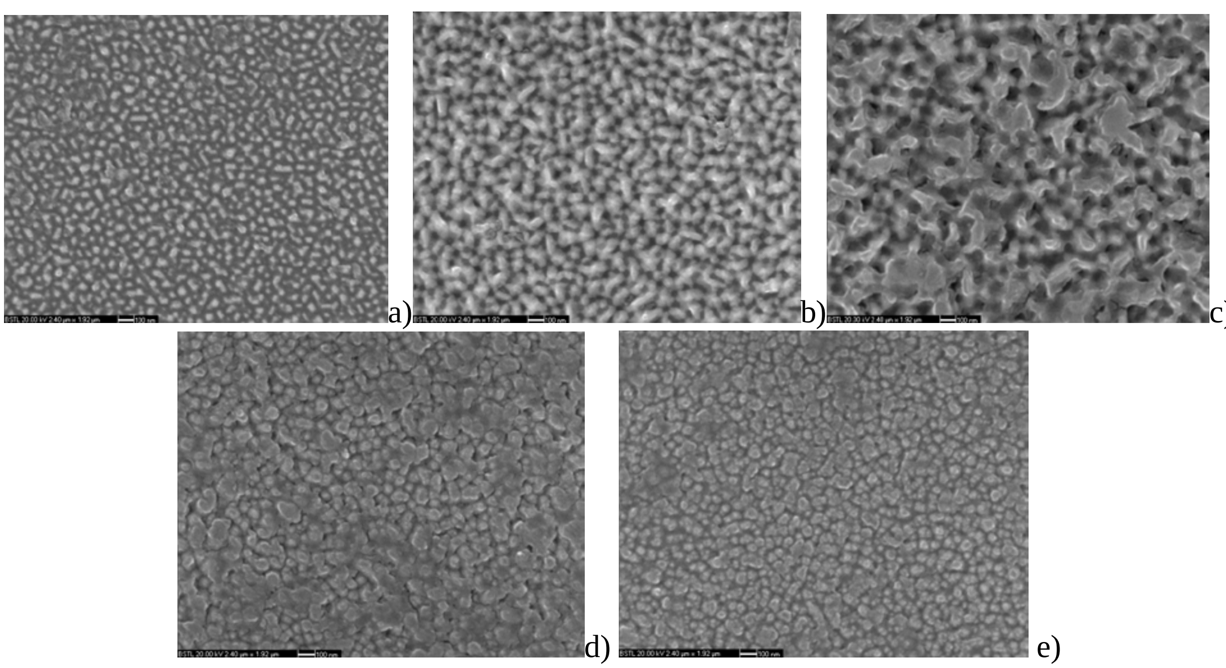

Fig. 2. SEM images of InN layers grown by MOCVD conventional mode (a), pulsed mode at temperatures 580 C^0 (b) and 600 C^0 (c), InGaN layers grown by pulsed mode with 80% (d) and 68% (e) of In.

dimensional InN film on GaN to a few bilayers, only. A 3D relaxed SK growth mode (islanding initiated) in nitrogen saturated ambient takes place [16]. Also extra strain can been relieved by dislocations. After some time, then the layer thickness reaches certain value some islands formed by SK growth mode become ripened: the excess material contributes to the formation of these islands instead of all islands and wetting film under it [17]. This effect explains the obvious differences of diameters from island to island. The situation in the case of In-rich InGaN layers is similar. The islanding effect and subsequent coalescence is shown by SEM (backscattered detector) images of InN and InGaN layers grown by conventional and pulsed MOCVD mode at different temperatures (Fig. 2). All samples were free of metallic In micro-droplets. The sample grown by conventional method at 580°C consisted of small and closely packed islands with diameter (50÷80) nm (Fig. 2 a). Grown by pulsed mode at the same growth temperature InN sample demonstrated slightly larger size of island (~100 nm) (Fig. 2 b). Growth at higher temperature (600°C) resulted into even larger islands (100÷500 nm) (Fig. 2 c). The island density in In-rich InGaN layers (80%, 68%) was very similar and the diameter varied from 50 to 150 nm (Fig. 2 d-e). Lower temperatures reduced the diffusion of atoms in the nucleation process defining high concentration of small islands, what worsened the optical and electrical properties of the layer. Differently, higher temperatures enhanced the diffusion of reactant species and resulted into larger islands, hence, better optical and electrical quality. Different size of islands influenced by temperatures was already observed for both growth modes [18,19]. The rougher surface with larger islands could be related to enhanced dissociation of InN [20]. Especially it becomes weighty for InGaN at elevated temperatures.

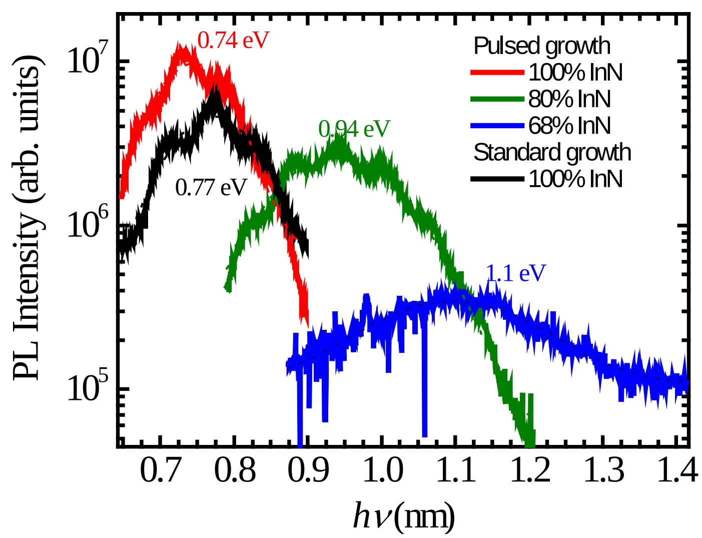

Fig. 3. Photoluminescence spectra of InN and In-rich InGaN layers grown on GaN/sapphire substrates by conventional and pulsed growth method.

PL signal at room temperature were detected for all InN and In-rich InGaN samples. The spectra were modulated by Fabry-Perot interferences in the ~3.5 μm thick GaN layer, which is transparent for band-to-band emission from InN. The emission maximum of the sample grown by conventional mode was found at 0.77 eV. It is slightly shifted to higher energies compared values reported in literature for pure InN (0.7 eV), e.g., [1]. This is attributed to the Burstein–Moss effect, since conduction band minima states are populated by background electrons [13]. The InN layer grown by pulsed method showed a PL signal with an amplitude being about 2 times higher. The Burstein-Moss shift (E_p = 0.74 eV) was smaller, what is consistent with the reduced background electron density in this layer. A drop of photoluminescence intensity with increasing Ga composition in InGaN layers was related to the increase of non-radiative recombination channel density caused by the increased amount of crystal defects. The increased line width of the spectrum is assigned to bandgap fluctuation caused by inhomogeneous In and Ga distribution in the layers. Nevertheless, the single PL peaks confirmed the XRD results (cf. Fig. 1) – the absence of phase separation.

Despite the problem with suitable (lattice-matched) substrates for InN and In-rich InGaN material, this alloy tends to have some other difficulties related with some forms of phase separations under the growth and some other issues originated from MOCVD processes.

One of the main problems for MOCVD growth of nitrides with high In content is enhanced thermal decomposition [21]. The bonds between indium and nitrogen are weaker than that of gallium and nitrogen, so less thermal energy is required to break these bonds. For example, in similar ambient and specific growth temperatures activation energy for InN is E_A=1.15 eV at T>595°C [22], while for GaN is E_A=3.62 eV at T<900°C [23]. In fact, besides complete bulk InGaN alloy decomposition, too high temperature creates point defects in the crystal what worsens optical and electrical properties of the layer. On the other hand, too low growth temperature suppresses precursor decomposition. In the case of pulse mode with enhanced surface reactant atom mobility the growth temperature could be reduced down to a certain level, while appropriate selection of pulse time duration of metalorganic supply allows to increase V/III ratios in order to avoid metal In droplet formation and to suppress the creation of numerous nitrogen vacancies.

InGaN alloys have a gap between pure GaN and InN when at certain temperature and metal composition during the growth phase separation occurs without any energy barrier [24]. This effect is called spinodal alloy decomposition. It has significant influence in the case of thick InGaN layers with more than 10% of In [25], but not for coherent thin layers under big compressive strain [26]. The pulse growth mode cannot prevent spinodal decomposition process, but can help to grow nanometric thickness films more accurate without pronounced thickness fluctuations.

Another natural process reducing crystal quality of alloys in the growth process is In segregation, witch can be vertical or lateral. Vertical segregation takes place due to different energy necessary for occupation of surface sites, where more favorable conditions are for Ga [27]. Lateral segregation of In can be explained by more stabile In-In bonds in comparison to In-Ga bonds [28]. In the latter case In aggregates into islands, if atoms are sufficient mobile at the surface and the amount of active nitrogen in growth zone is low [29]. In the pulse mode pausing provides extra time for nitridization and In migration at the surface, what suppresses In segregation.

For a better understanding of the processes occurring during pulsed MOCVD growth, further specific analysis and appropriate theoretical modeling are needed.

4. Conclusion

We succeeded to grow metal droplet-free InN and In rich InGaN layer on GaN templates using pulsed MOCVD mode. The incorporation of In and Ga was confirmed by XRD measurements. All layers demonstrated room temperature photoluminescence. Relative high electron mobility μ_e = 644 cm^2/(Vs) and low background electron concentration n_e=8·10^{18} cm^{-3}

were obtained for InN layer grown at a temperature of 600ºC. Photoluminescence peak of InN layer with small Burstein-Moss shift was observed at 0.74 eV (0.7 eV for pure InN). The absence of phase separation in In-rich InGaN layers was confirmed by single peak behavior in photoluminescence and in XRD $\omega/2\Theta$ scans. Pulsed MOCVD mode has been successfully introduced for the growth of InGaN for the entire composition range.

Acknowledgements

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