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A. V. Sampath
US Army Research Laboratory, anand.sampath@us.army.mil

G. A. Garrett
US Army Research Laboratory

E. D. Readinger
US Army Research Laboratory

R. W. Enck
US Army Research Laboratory

H. Shen
US Army Research Laboratory

See next page for additional authors

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A.V. Sampath [a,*], G.A. Garrett [a], E.D. Readinger [a], R.W. Enck [a], H. Shen [a], M. Wraback [a], J.R. Grandusky [b], L.J. Schowalter [b]

[a] US Army Research Laboratory, RDRL-SEE-M, 2800 Powder Mill Road, Adelphi, MD 20783, United States
[b] Crystal IS, Inc., 70 Cohoes Avenue, Green Island, NY 12183, United States

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ABSTRACT

The optical and structural properties of AlGaN active regions containing nanoscale compositional inhomogeneities (NCI) grown on low dislocation density bulk AlN substrates are reported. These substrates are found to improve the internal quantum efficiency and structural quality of NCI-AlGaN active regions for high Al content alloys, as well as the interfaces of the NCI with the surrounding wider bandgap matrix, as manifested in the absence of any significant long decay component of the low temperature radiative lifetime, which is well characterized by a single exponential photoluminescence decay with a 330 ps time constant. However, room temperature results indicate that non-radiative recombination associated with the high point defect density becomes a limiting factor in these films even at low dislocation densities for larger AlN mole fractions.

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1. Introduction

Despite the recent progress in the development of III-Nitride semiconductor based deep ultraviolet light emitting diodes (DUVLEDs), commercially available devices emitting at wavelengths shorter than 280 nm still suffer from poor wall plug efficiencies on the order of ~1% [1]. One factor limiting the performance of these devices is the presence of a large density of dislocations arising from the typical heteroepitaxial growth on *c*-plane sapphire substrates that are linked to a high non-radiative recombination rate. Previously, we have reported on the growth of AlGaN active regions containing self-assembled nanometer scale compositional inhomogeneities (NCI-AlGaN) that demonstrate enhanced luminescence efficiency despite the presence of a large dislocation density [2]. This phenomenon is attributed to: (1) the high density of NCI regions that improves the probability of carriers recombining radiatively within them rather than non-radiatively at a structural defect and (2) the subsequent concentration of carriers within the narrower band gap NCI regions that suppresses non-radiative recombination and enhances radiative efficiency due to the reduced radiative lifetime at high carrier density [3,4]. Nevertheless, time-resolved photoluminescence (TRPL) studies show that the reduction of dislocation density in these materials further improves LED active region performance, as characterized by an enhancement of the internal quantum efficiency (IQE) and the room temperature PL lifetime by ~2× [5], a phenomenon that may be due to improved transport from the wider bandgap matrix to the NCI and concomitant higher carrier concentration therein. Bulk AlN has significant advantages over conventional *c*-plane sapphire as a substrate for III-Nitride based DUVLEDs, including a low dislocation density (etch pit density <10^4 cm^{-2}), a reduced lattice mismatch, a high thermal conductivity, and a high transparency at wavelengths of interest. In this paper we report on the optical and structural properties of NCI-AlGaN films grown directly on bulk AlN substrates. In particular, we show a link between improved structural quality and longer non-radiative lifetime at room temperature, as well as suppression of deleterious long radiative lifetime components at low temperature associated with localization at interface fluctuations.

2. Experimental method

The samples grown on bulk AlN substrates consisted of a 600 nm thick, 70% AlN mole fraction, NCI-AlGaN film deposited directly on the substrates by plasma assisted molecular beam epitaxy using conditions published elsewhere [6]. Prior to introduction into the reactor, the N-polar backsides of the substrates were sputter coated with a ~2 μm thick Ti film to improve heating uniformity, which was then capped with a protective SiO_2

* Corresponding author. Tel.: +1 3013940104; fax: +1 3013940310.
E-mail address: anand.sampath@us.army.mil (A.V. Sampath).

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layer to prevent damage to the film during chemical preparation. Chemical preparation was performed immediately prior to loading the substrates into the reactor and consisted of solvent degreasing followed by etching in a 3:1 HCl:HNO_3 solution heated to 80 °C for ~10 min and then removal of the SiO_2 cap by dipping in BOE for 30 s. Finally, the substrates were prepared *in situ* by annealing the substrate at the growth temperature of 900 °C while periodically covering the surface with Ga metal and then allowing the film to evaporate to remove surface oxides [7].

The optical properties of the samples were investigated by temperature dependent cw-photoluminescence using a 244 nm Coherent FReD Argon Ion Laser with a low output power of ~0.5 mW so as to avoid effects associated with the saturation of defects or photo-bleaching that can result from the excitation of a large density of photogenerated carriers. The samples were cooled to ~8 K using a cryostat and a closed-cycle He compressor. The photoluminescence lifetimes of the heterostructures were measured by time-correlated single photon counting with ~25 ps resolution using a broadly tunable (230–375 nm) frequency doubled femtosecond optical parametric amplifier as the excitation source. The structural properties of the samples were investigated by X-ray diffraction using a Panalytical Xpert MRD diffractometer.

3. Results

X-ray diffraction (XRD) studies were employed to assess the improvement in the structural quality of the 70% NCI-AlGaN films grown on bulk AlN substrates. Fig. 1 shows a reciprocal space map (RSM) of the NCI-AlGaN film along the asymmetric (1 0–1 4) direction that provides information on both the in-plane and out-of-plane lattice constants and therefore the strain state of the film. Specifically, the wurtzite lattice constants *a* and *c* are related to the reciprocal lattice points Q_x and Q_y by the relations $a = (2\pi/Qx)^{ast}(4/3(h^2+k^2+hk))^{1/2}$ and $c = 2\pi^* l/Q_y$ [8,9]. Therefore vertical lines in the RSM represent lines of constant *a* lattice parameter and the degree of relaxation in the film may be calculated as $R = [a(L) - a_0(S)]/[a_0(L) - a_0(S)]$ where $a(L)$ and $a_0(L)$ are the measured and relaxed *a* lattice constants of the alloy and $a_0(S)$ is the relaxed lattice constant of the substrate [8]. The narrow, intense peak in the top of the RSM map corresponds to the AlN substrate, while the broader peak in the bottom of the plot corresponds to the NCI-AlGaN layer deposited on top. The RSM reveals that the 600 nm thick 70% NCI-AlGaN film is highly strained to the AlN substrate with the degree of relaxation estimated to be ~12.9%. This result is consistent with those of Grandusky et al., who have reported on the ability to grow AlGaN films with AlN mole fractions >60% pseudomorphically on bulk AlN substrates, with layer thicknesses between 0.5 and 1 μm that are significantly greater than the critical thickness predicted by the Matthews–Blakeslee model [10]. As a result, these pseudomorphic AlGaN films are expected to replicate the structure of the bulk AlN substrate without the formation of dislocations. Therefore, the highly strained NCI-AlGaN film grown on bulk AlN is expected to contain a significantly lower dislocation density than similar fully relaxed films grown on *c*-plane sapphire or templates consisting of thin III-Nitride layers grown on *c*-plane sapphire. It should be noted that other groups have reported on strain relaxation in high AlN mole fraction films (>60%) grown on sapphire or SiC substrates through the formation of dislocations [11,12] in contrast to what we observe for growth of these films on bulk AlN. Understanding this result in terms of the differences in the strain relaxation mechanisms between the AlGaN/ bulk AlN system and the more commonly investigated AlGaN/AlN/*c*-plane sapphire system requires further investigation. The full width at half maximum (FWHM) of the XRD rocking curves along the (0 0 0 2) and (1 0–1 4) directions

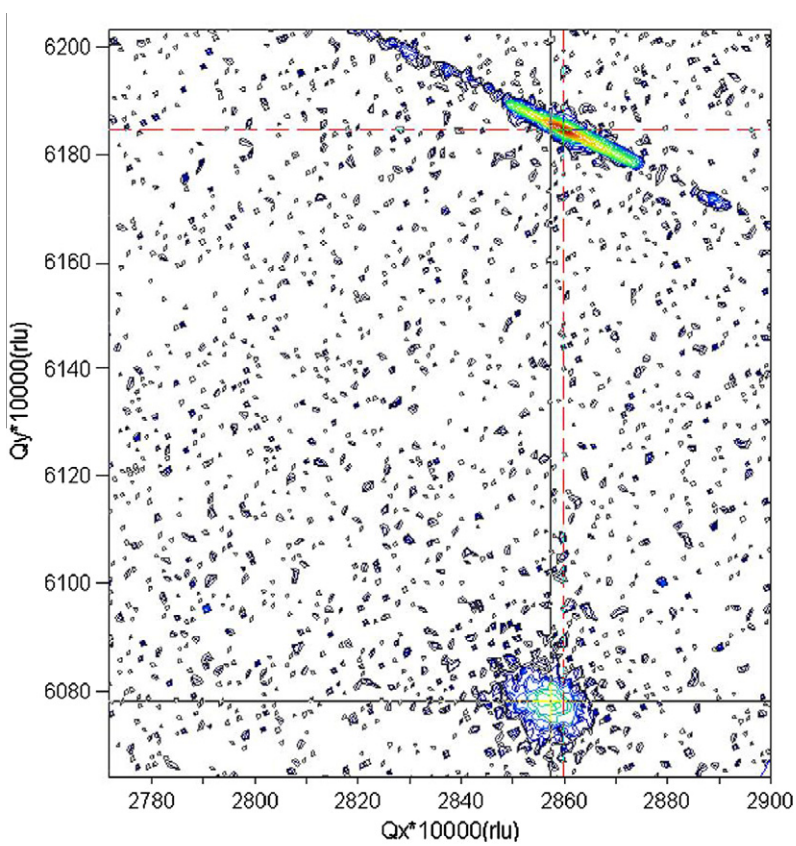

Fig. 1. (1 0–1 4) Reciprocal space map for NCI-AlGaN film on bulk AlN substrate.

were observed to be 150″ and 250″, respectively, attesting to the epi-readiness of the surface of the bulk AlN substrate while representing a significant improvement over films grown directly on *c*-plane sapphire. However, these results are more comparable to fully relaxed AlGaN films investigated by Gradusky et al. rather than pseudomorphic AlGaN films that exhibited FWHM of the XRD rocking curve in the (0 0 0 2) and (1 0–1 2) directions of 81″ and ~105″, respectively [10]. While some of this broadening is likely related to the formation of dislocations at the heterointerface, it may also be partially attributed to the presence of the compositional inhomogeneities in the NCI-AlGaN films.

The room temperature and low temperature (8 K) cw photoluminescence (cw-PL) spectra for a typical 600 nm thick 70% NCI-AlGaN film deposited on a bulk AlN substrate with room temperature emission at ~272 nm are shown in Fig. 2. For comparison, the corresponding cw-PL spectra for a NCI-AlGaN single heterostructure (NCI-AlGaN-SH) consisting of a 80 nm thick NCI-AlGaN active region deposited upon a 2.3 μm thick, Si doped AlGaN template grown by metalorganic chemical vapor deposition (MOCVD) and having 51% AlN by mole fraction are also shown. The PL emission spectrum of this structure peaks at 292 nm. The internal quantum efficiency, as estimated by the ratio of the integrated cw-PL intensity measured at room temperature and 8 K, increases from 26% for the NCI-AlGaN-SH to 34% for the film grown on the bulk AlN substrate. The room temperature time-resolved photoluminescence (TRPL) studies of both structures are shown in Fig. 3. The photogenerated carrier lifetime in the NCI-AlGaN film grown on the bulk AlN substrate is 220 ps, which is ~25% longer than that in the NCI-AlGaN-SH, 175 ps.

Temperature dependent TRPL studies of the NCI-AlGaN film grown on bulk AlN and the NCI-AlGaN-SH are shown in Fig. 4. The photogenerated carrier lifetimes in both films decrease monotonically with increasing temperature, suggesting that non-radiative recombination limits their performance at room temperature. TRPL studies of the film on bulk AlN at low temperature, where non-radiative channels are frozen out, reveals a short radiative lifetime of ~330 ps, which is faster than what we observe for the NCI-AlGaN-SH, ~444 ps, as well as faster than what we have previously observed for high quality multiple quantum well based active regions in commercially available LEDs on sapphire at similar emission wavelength [13].

4. Discussion

The enhancement in the integrated cw-PL intensity observed for the NCI-AlGaN film deposited on a bulk AlN substrate over that found for the NCI-AlGaN-SH, whose dislocation density is estimated to be $\sim10^8\ cm^{-2}$ by transmission electron microscopy, is consistent with a reduction in the dislocation density in this film owing to a reduced lattice mismatch and a concomitant reduced strain relaxation that suppresses dislocation formation. The observed increase in IQE, from 26% for the NCI-AlGaN-SH to 34% for the film grown on the bulk AlN substrate, as well as the longer room temperature PL lifetime, which primarily tracks the non-radiative lifetime, for the film grown on the bulk AlN substrate provides further support for this interpretation (Table 1). As non-radiative recombination channels are frozen out at low temperature, the TRPL signature becomes more representative of the radiative lifetime. While the dominant component of this radiative lifetime is expected to become shorter with increasing Al content due to the larger exciton binding energy and concomitant oscillator strength, the extended decay in the TRPL observed at low temperature, which may be associated with a longer radiative lifetime related to carrier localization due to fluctuation of the NCI/matrix interfaces, is significantly suppressed in the films grown on the bulk AlN substrate compared to that of the NCI-AlGaN-SH or the high quality multiple quantum well samples on sapphire [13]. Taken together, these observations suggest improved structural quality related to the high quality bulk AlN substrate employed has a beneficial effect on non-radiative recombination rates at room temperature in the NCI-AlGaN films.

However, this enhancement in the room temperature optical properties of the NCI-AlGaN films on bulk AlN over those in the

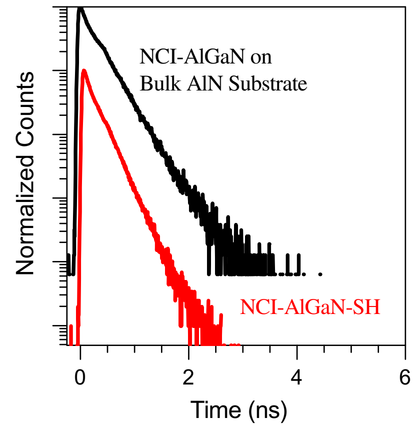

Fig. 3. Room temperature TRPL data for NCI-AlGaN film on bulk AlN substrate and NCI-AlGaN-SH on MOCVD template .

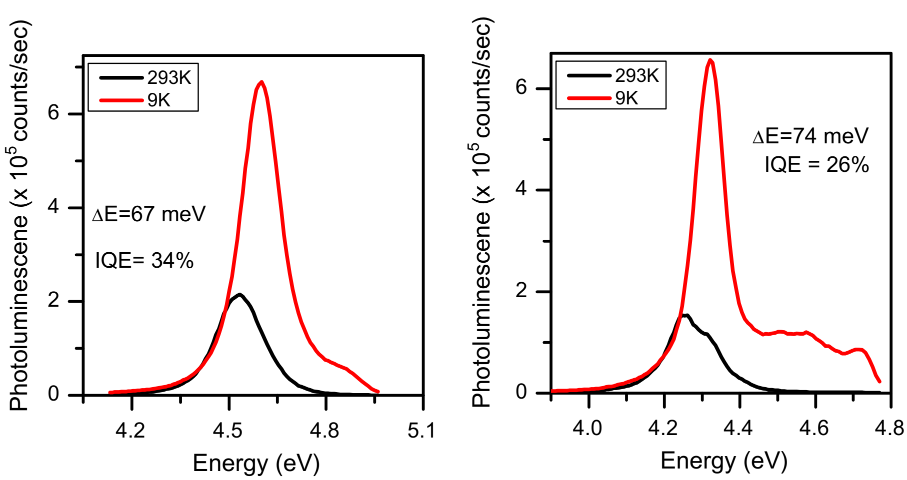

Fig. 2. Room temperature and low temperature cw-PL spectra for NCI-AlGaN film on bulk AlN substrate (left) and NCI-AlGaN-SH on MOCVD template (right).

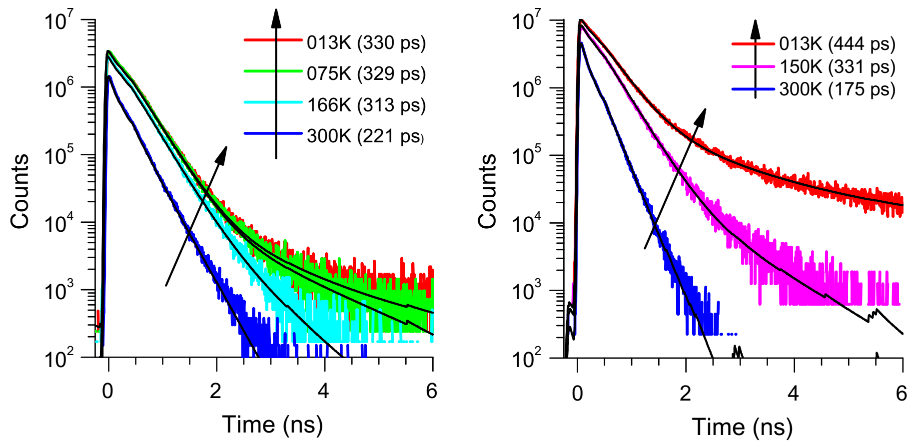

Fig. 4. Temperature dependent TRPL data for NCI-AlGaN film on bulk AlN substrate (left) and NCI-AlGaN-SH on MOCVD template (right).

Table 1
Optical and structural properties of investigated NCI-AlGaN films.

NCI-AlGaN sample	Matrix AlN mole fraction (%)	Dislocation density (cm^{-2})	IQE (%)	τ_{PL} @ 293 K (ps)	τ_{PL} @ 8 K (ps)
On bulk AlN	70	$\ll 10^8$	34	220	330
SH	51	$\sim 10^8$	26	175	444
DH	33	$\sim 10^{10}$	30	530	439

NCI-AlGaN-SH appears incommensurate with the dislocation density reduction due to the bulk AlN substrate. While the ~25–30% improvement in the IQE and room temperature TRPL lifetime for the NCI-AlGaN film on bulk AlN as compared to the NCI-AlGaN-SH may indicate only moderate structural improvement arising from the partial relaxation of the former, another explanation may be found through comparison with an NCI-AlGaN double heterostructure (DH) active region having only 33% AlN by mole fraction but a larger dislocation density due to the AlGaN template employed as the substrate (Table 1). This DH exhibits an IQE of 30% and a long PL lifetime of ~530 ps at room temperature that is primarily indicative of a long non-radiative lifetime due to localization of carriers in the NCI away from dislocations and saturation of the non-radiative centers within the NCI associated with the high carrier concentration in the NCI [3,4]. Further support for this interpretation is seen in the observed shortening of the photogenerated carrier lifetime at low temperature, where the radiative lifetime dominates. In contrast, the NCI-AlGaN film grown on the bulk AlN substrate exhibits a significantly shorter room temperature photogenerated carrier lifetime of ~220 ps despite having over two orders of magnitude lower dislocation density. While the IQE in these two films may be similar because of the large difference in radiative lifetime (~650 ps for the film on bulk AlN versus ~2 ns for the lower Al content DH at room temperature) attributed to the increase in the exciton binding energy with increasing AlN mole fraction, the decrease in PL lifetime with increasing temperature for the film on bulk AlN suggests that non-radiative recombination limits the PL lifetime, since the radiative lifetime is expected to increase with increasing temperature in the absence of significant quantum confinement in the NCI. The observed shortening of the PL lifetime with increasing AlN mole fraction is therefore more likely related to a significant concomitant increase in the density of point defects that compete effectively with the density of NCI regions in these films and partially mitigate the suppression of non-radiative recombination by the NCI. These point defects may be associated with the increased Al in the films, which is known to getter impurities such as oxygen that are manifested as deep levels.

5. Conclusions

We have examined the structural and optical properties of AlGaN films containing compositional inhomogeneities on high quality, low defect density, bulk AlN substrates. These substrates are found to improve the internal quantum efficiency and structural quality of NCI-AlGaN active regions for high Al content alloys, as well as the interfaces of the NCI with the surrounding wider bandgap matrix, as manifested in the absence of any significant long decay component of the low temperature radiative lifetime, which is well characterized by a single exponential photoluminescence decay with a 330 ps time constant. The structural improvement of NCI-AlGaN films grown on a bulk AlN substrate is attributed to reduced lattice mismatch and strain relaxation in the NCI-AlGaN films that inhibit the formation of dislocations. While improved structural quality related to the high quality bulk AlN substrate employed has a beneficial effect on non-radiative recombination rates at room temperature in the NCI-AlGaN films, the increasing density of point defects and impurities in these films with increasing AlN mole fraction are found to limit their performance as deep UV LED active regions, although less so than in comparable conventional structures due to the combination of low dislocation density and NCI.

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