Effect of indium in Al$_{0.65}$Ga$_{0.35}$N/Al$_{0.8}$Ga$_{0.2}$N MQWs for the development of deep-UV laser structures in the form of graded-index separate confinement heterostructure (GRINSCH)

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AlGaN-based graded-index-separate-confinement-heterostructures (GRINSCHs) with Al$_{0.65}$Ga$_{0.35}$N/Al$_{0.8}$Ga$_{0.2}$N MQWs in their active region were grown by plasma-assisted MBE on (0001) 6H-SiC substrates. The MQWs were grown under excess Ga. Indium flux was used in addition in some of the samples in order to study the role of indium on the growth mode of such MQWs. Transmission electron microscopy (TEM) provides evidence that the bottom compositionally graded AlGaN layer in the GRINSCH structure may also be serving as a strain transition buffer layer, by blocking threading defects in the vicinity of the AlN/AlGaN heterointerface. X-ray diffraction (XRD) indicates that the interfaces in the MQWs grown in the presence of indium are sharper. However, photoluminescence (PL) studies indicate evidence of stimulated emission at relatively low threshold only in the sample grown without indium, which is attributed to deep band structure potential fluctuations in this sample. The presence of indium during growth led to more homogeneous AlGaN MQWs, which require higher excitation flux to produce population inversion.

1 Introduction The development of AlGaN-based UV optoelectronic devices (emitters, detectors, and electro-absorption modulators) has been an active area of research over the past two decades [1–4]. This research is motivated by a plethora of potential industrial applications. These include, for example, free-space non-line-of-sight communications, water/air/food sterilization, surface disinfection, and fluorescence or Raman identification of biological/chemical agents. AlGaN alloys are well suited for such devices because their energy gap can be tuned by changing the alloy composition to cover the entire UV spectral region from 210 to 360 nm. However, despite intense efforts worldwide, the maximum external quantum efficiency (EQE) of fully packaged AlGaN-based deep-UV LEDs emitting below 300 nm is only 1–3% [4–8]. Only recently Shatalov and co-workers reported a UV LED emitting at 278 nm with EQE of about 10% [9]. This is to be contrasted with InGaN–based violet-blue LEDs, whose EQE is more than 50% [10]. The development of AlGaN-based UV lasers is at an even earlier stage. Several groups have reported the development of optically pumped deep UV lasers [11–13]. However, the shortest reported wavelength of electrically pumped UV lasers is 336 nm [14].

There are a number of fundamental problems with AlGaN alloys, which are responsible for the relatively low progress in developing efficient deep UV optoelectronic
devices. Specifically, during heteroepitaxial growth of AlGaN alloys, active nitrogen, produced either by thermal decomposition of ammonia in metalorganic chemical vapor deposition (MOCVD) or by plasma decomposition of molecular nitrogen in molecular beam epitaxy (MBE), is chemically very active and reacts instantly with arriving Al atoms and limits their diffusivity. This leads to AlGaN films with microstructures consisting of small hexagonal columnar domains. Such materials are expected to have high dislocation density, since the threading dislocations occur primarily at the boundaries of the hexagonal columnar domains due to their incomplete coalescence [15]. Furthermore, coalescence of the small domains leads to tensile stress, which promotes nucleation and propagation of cracks [16]. This is even more important in silicon-doped high Al content AlGaN films, since silicon acts as anti-surfactant and thus leads to microstructures with even smaller domains [17]. Another source of the poor internal quantum efficiency (IQE) of deep UV LEDs is the incorporation of oxygen in AlGaN due to the high chemical affinity of aluminum for oxygen [18–20]. While oxygen is a shallow donor in GaN and InGaN alloys, it is known to form DX-like states in AlGaN alloys with high AlN mole fraction [21]. Other potential problems are the poor doping efficiency of AlGaN with high AlN mole fraction, which is responsible for the poor carrier injection in the active region of the device [22]. Furthermore, there are difficulties in light extraction due to emission selection rules originating from changes in the valence band structure of AlGaN alloys as the AlN mole fraction in the alloy increases [23].

Various approaches are currently been pursued to address these problems. A number of groups are developing deep UV emitters (LEDs and lasers) by growing such devices pseudomorphically on AlN substrates [8, 12, 13]. However, such substrates are currently available in small sizes and are prohibitively expensive. Some groups have employed indium as a surfactant to promote two-dimensional (2D) growth during deposition of AlGaN alloys under slightly N-rich conditions [24–26]. Our group’s approach is to deposit AlGaN alloys by plasma-assisted MBE heteroepitaxially on traditional substrates (sapphire, SiC) under excess Ga than required for stoichiometric growth, since the composition of the AlGaN alloys is determined only by the ratio of the Al-flux versus the flux of the active nitrogen [27]. This growth techniques introduces deep band structure potential fluctuations, where the injected electron-hole pairs are localized leading to efficient radiative recombination [15, 17, 19, 20, 28–34]. Using such growth methods we have demonstrated the formation of AlGaN multiple quantum wells (MQWs) emitting at 240–250 nm with IQE as high as 70% [30]. Furthermore we have shown that such AlGaN quantum wells have a net modal optical gain in excess of 118 cm\(^{-1}\) with very low transparency threshold of 5 \(\mu\)J cm\(^{-2}\), which corresponds to 1.4 \(\times\) 10\(^{17}\) cm\(^{-2}\) excited carriers [31–33].

To address the issues of poor doping of such alloys, as well as to increase the confinement factor of the optical mode in deep UV lasers we have recently proposed the growth of these devices in the form of graded-index-separate-confinement-heterostructure (GRINSCH) [34]. In such a structure, the compositionally graded regions of AlGaN in either side of the active region are doped by polarization n- and p-type, respectively [35], while simultaneously they increase the confinement of the optical mode due to variation of the index of refraction of the compositionally graded AlGaN films [34, 36–39].

In this paper, we compare the growth, the crystal structure, and the optical properties of two deep-UV-emitting AlGaN-based GRINSCH structures, grown by plasma-assisted MBE. In the first structure the active region, consisting of AlGaN QWs, was grown under excess Ga than required for stoichiometric growth. The second structure was identical to the first one, but during the growth of the AlGaN MQWs an indium flux was also used in order to investigate whether indium has the same effect as during growth of AlGaN alloys under slightly N-rich conditions.

2 Experimental

The two types of deep UV emitting AlGaN-based GRINSCH structures were grown by plasma-assisted MBE on the Si-face of 6H-SiC substrates. The MBE system is equipped with an EPI rf plasma source for nitrogen activation and traditional effusion cells for the vaporization of Al, Ga, and In. The substrate preparation and film growth were monitored by reflection-high-energy-electron diffraction (RHEED) at 10 keV electron energy. The SiC substrates were first carefully cleaned \textit{ex situ} in organic solvents followed by dipping into heated piranha etch and then buffered HF to remove surface contaminants and oxides. In addition, the substrates were cleaned \textit{in situ} by exposure to Ga flux at 750 °C for complete Ga coverage followed by fast heating to 850 °C for Ga desorption. This process was found to lead to a sharp RHEED pattern, which is attributed to the removal of oxygen, carbon, hydrogen, and other physically absorbed or chemisorbed impurities through the formation of volatile Ga-compounds. The substrate temperature during growth of the AlGaN QWs and the AlGaN graded regions was kept at 780°C.

The two investigated structures are schematically shown in Fig. 1. The active region consists of 10 A\(_{0.65}\)GaN\(_{0.35}\)N...
(1.5 nm)/Al_{0.8}Ga_{0.2}N (3 nm) MQWs sandwiched between two 50 nm thick compositionally graded Al_{x}Ga_{1-x}N films ($x = 1–0.8$ and $x = 0.8–1$). The two structures are identical except in the one structure (sample A) we did not employ indium during the growth of the quantum wells, while in the second structure (sample B) we did use an indium flux of $2 \times 10^{-6}$ Torr during the growth of the quantum wells. The wells of both structures were grown under excess gallium, to promote band structure potential fluctuations as described previously.

The structure and microstructure of the two samples were investigated by transmission electron microscopy (TEM) and X-ray diffraction (XRD). The samples for TEM studies were prepared by standard mechanical polishing followed by ion-beam-thinning at 4.5 keV. Conventional diffraction-contrast images and high-resolution phase contrast images were recorded with a JEM 4000EX high resolution electron microscope equipped with a top-entry, double tilt specimen holder operated at 400 keV. The samples were also investigated by on-axis $\theta–2\theta$ X-ray diffraction (XRD) scans using a Philips four-circle high-resolution diffractometer.

The optical properties of these samples were investigated under femtosecond optical pumping. The samples were excited with 220 nm, 150 fs laser pulses obtained by pumping a proper crystal (Spectra Physics GWU-24FL) with a mode-locked ultra-fast high-power Ti:sapphire laser (SpectraPhysics MaiTai, 82 MHz) operating at 880 nm. The laser pulses were focused on the sample surface through a cylindrical lens. The pumping fluence on the sample was varied up to $80 \mu$J cm$^{-2}$. The photoluminescence (PL) was collected from the cleaved edge of the sample through an UV-transmitting objective, a UV-transmitting movable analyzer, a computer-controlled $1/4$ monochromator (Cornerstone 260) with UV-efficient gratings, and a lock-in amplifier (Oriel Merlin) coupled to a UV-optimized photomultiplier tube (Oriel Instruments 77348).

3 Experimental results and discussion

Figure 2 shows a cross-sectional electron micrograph of the sample grown without indium. High density of threading dislocations (TDs) was formed at the nucleation interface between AlN and SiC and they propagate along the growth direction. However, many of the TDs terminate at the AlN/graded AlGaN layer, as shown in the image at the left. The likely cause for the dislocation termination at this interface is the strain associated with the compositionally graded AlGaN wave guiding film. Thus, the graded AlGaN film not only provides strong optical and carrier confinement, but it also relieves strain between the cladding AlN layer and the active layer by serving as a strain transition buffer. These results indicate that the compositionally graded AlGaN layer with an optimum thickness and growth condition can effectively block the TDs in the vicinity of the AlN/AlGaN heterointerface and reduce the density of TDs present in the active layer [34]. As indicated in the enlarged image to the right of Fig. 2, the Al$_{0.65}$Ga$_{0.35}$N/Al$_{0.8}$Ga$_{0.2}$N layers are well formed with relatively abrupt interfaces.

Figure 3 shows the XRD $\theta–2\theta$ diffraction patterns for the two investigated samples. The XRD simulation results of the MQW structure are also shown in the same figure. The blue line indicates the XRD scan of sample grown without indium present during growth of the quantum wells, while the black line represents the one grown with indium. The main superlattice diffraction (SL-0) for both samples occurs on the left shoulder of the SiC diffraction peak. While the simulations indicate the existence of one superlattice peak in the scanned area, the experimental results indicate only a small superlattice (SL-1) peak in the sample whose QWs were grown with indium. The magnitude of this superlattice (SL-1) peak is two orders of magnitude smaller than the main superlattice peak (SL-0), which is the same as the ratio of the two corresponding peaks in the simulation results. This small intensity or complete absence of superlattice peaks in the experimental data is to be expected because of the small difference in the composition of the wells and

Figure 2 TEM cross-sectional micrograph of the GRINSCH structure with QWs grown without indium. A number of threading defects in the AlN are terminated in the interface of AlN/graded AlGaN interface.

Figure 3 XRD diffraction of the two types of investigated GRINSCH structures. The data suggest that the presence of indium leads to QWs with sharper interfaces.
barriers in addition to unavoidable interface roughness. These results imply that the MQWs of the sample grown with indium have sharper interfaces, which is consistent with indium being a surfactant during the growth of the MQWs as discussed by Monroy et al. [24].

Figure 4a shows the PL spectra of the two investigated samples. The excitation intensity was 60 μJ cm\(^{-2}\) and PL spectra were taken at room temperature. Both samples show a single peak. The sample with indium present during the growth of the quantum wells has a peak at 270.5 nm, and the sample grown without indium has a peak at 272.3 nm. Thus, the presence of indium resulted in a small blue shift of the PL spectra and a slight reduction in the PL intensity. Both of these results indicate that the presence of indium improved the homogeneity of the sample as also discussed in Ref. [33] using monochromatic cathodoluminescence measurements. In other words, the QWs grown with indium have shallower potential fluctuations which are responsible both for the blue shift of the spectra as well as the reduction in the PL intensity.

Figure 4b and c show the amplified spontaneous emission (ASE) peak intensity as a function of the pump fluence for the two investigated samples. The ASE intensity of the sample grown with indium in the QWs shows a linear dependence at low fluence and sub-linear dependence for pumping fluence higher than 30 μJ cm\(^{-2}\). In contrast, the ASE intensity exhibits a clear super-linear dependence in the sample grown without indium in the MQWs. The superlinear emission along with the blue shift and spectral narrowing, which was reported in Ref. [33] for similar AlGaN QWs, provide strong evidence of stimulating emission in this sample. The low transparency threshold of about 10 μJ cm\(^{-2}\) is attributed to deep potential fluctuations introduced by compositional inhomogeneities in the AlGaN films grown under Ga-rich condition [31, 33]. The stimulated emission of the sample grown without indium at relatively low threshold is attributed to population inversion of the potential fluctuations rather than of the entire AlGaN matrix. As reported in Ref. [33], the presence of indium flux during growth of the QW leads to more homogeneous material, which requires higher fluence than available in our experimental apparatus to induce population inversion.

As discussed previously the XRD data are consistent with the notion that indium acts as a surfactant even during Ga-rich conditions of growth as is the case under slightly N-rich conditions of growth [24]. The optical data on the other hand indicate that the presence of indium during the growth of the AlGaN QWs leads to more homogeneous material by removing compositional inhomogeneities, which otherwise give rise to band structure potential fluctuations. As discussed elsewhere [17, 19, 20], the growth mode of AlGaN under Ga-rich growth conditions is consistent with liquid phase epitaxy rather than physical vapor phase epitaxy and leads to lateral compositional inhomogeneities in the films due to statistical variations of the thickness of the liquid gallium in the surface. In this growth mode, indium dissolves in the liquid Ga at the surface of the growing film and forms In–Ga liquid solution [40], which based on the experimental data, appears to better wet the AlGaN seed under the In–Ga liquid solution. Thus, the In–Ga liquid solution is more uniform in thickness across the wafer and thus leads to more homogeneous composition AlGaN alloys. This model can also account for the sharp interfaces of the AlGaN QWs grown in the presence of indium. We do not have analytical data regarding indium incorporation in the AlGaN films, but it appears to be unlikely at the high growth temperature of 780 °C.

4 Conclusions In summary, we have investigated the role of indium in influencing the crystal growth/structure and optical properties of AlGaN MQWs embedded into a GRINSCH structure emitting at 270 nm. The TEM data indicate that the compositionally graded AlGaN layer is also serving as a strain transition buffer to block threading dislocations to penetrate into the MQWs. The XRD data
indicate that the AlGaN MQWs grown in the presence of indium have sharper interfaces between well and barriers, consistent with notion that indium is a surfactant [24]. In spite of that the sample grown without indium shows superlinear dependence on pump fluence providing evidence of stimulated emission. The superlinear behavior of the sample grown without indium is accounted for by the existence of deep band structure potential fluctuations [31, 33]. On the other hand, the sample grown with indium appears to be more homogeneous. We hypothesized that the indium dissolves into liquid Ga in the surface of the growing AlGaN film and forms Ga–In liquid solution that wets better the AlGaN seed and forms a liquid film of uniform thickness across the wafer. Thus, the composition of the resulting AlGaN films is more uniform across the wafer. Such compositionally uniform film will require higher pumping fluence to produce population inversion [33].

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References