Nanoselective area growth of defect-free thick indium-rich InGaN nanostructures on sacrificial ZnO templates

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Abstract
Nanoselective area growth (NSAG) by metal organic vapor phase epitaxy of high-quality InGaN nanopyramids on GaN-coated ZnO/c-sapphire is reported. Nanopyramids grown on epitaxial low-temperature GaN-on-ZnO are uniform and appear to be single crystalline, as well as free of dislocations and V-pits. They are also indium-rich (with homogeneous 22% indium incorporation) and relatively thick (100 nm). These properties make them comparable to nanostructures grown on GaN and AlN/Si templates, in terms of crystallinity, quality, morphology, chemical composition and thickness. Moreover, the ability to selectively etch away the ZnO allows for the potential lift-off and transfer of the InGaN/GaN nanopyramids onto alternative substrates, e.g. cheaper and/or flexible. This technology offers an attractive alternative to NSAG on AlN/Si as a platform for the fabrication of high quality, thick and indium-rich InGaN monocrystals suitable for cheap, flexible and tunable light-emitting diodes.

Keywords: InGaN, nano selective area growth—NSAG, metal organic vapor phase epitaxy—MOVPE, zinc oxide—ZnO

(Some figures may appear in colour only in the online journal)
templates) [8, 9]. These issues are even more pronounced in the case of InGaN growth on silicon, as reported by several authors who recently grew InGaN layers (with up to 40% of indium content) on AlN-buffered Si (111) substrates by plasma-assisted molecular beam epitaxy (PA-MBE) and metal organic vapor phase epitaxy (MOVPE) [10–13]. Moreover these silicon-based processes may have additional disadvantages, like a longer processing time due to the back-etching of the Si substrate, and the resulting impossibility to re-use the wafer [10–13]. Thus it is desirable to develop novel approaches to improve the quality of thick and indium-rich InGaN epilayers. One potential solution is in the growth of InGaN nano-structures using a non-adsorbing masking material which could accommodate the elastic strain without the generation of dislocations [14]. Significant work has been reported on self-assembled InGaN nanostructures over the entire composition range using HVPE, but this process leads to a random distribution of island sizes [15]. Others have reported MBE growth of InGaN nanostructures on GaN-nanocolumn-buffered silicon substrates emitting from the ultraviolet (3.2 eV) to the infrared (0.78 eV) and achieved an internal quantum efficiency of 36% for green-emitting nanocolumns [16]. Using MOVPE, low indium content InGaN nanostructures have been selectively grown only on GaN templates by pulsing the precursors [17]. Recently, using continuous flow MOVPE on GaN templates and an improved patterning process, the growth of thick, uniform, dense, single phase, indium-rich nanorod arrays was demonstrated on both GaN/c-sapphire [18, 19] and AlN/Si wafers [20]. ZnO substrates offer a number of advantages over c-sapphire, AlN/Si and wurtzite SiC wafers [21]: a lower lattice mismatch with GaN (1.8% versus respectively 16% and 4%), a lattice match with InGa0.22Ga0.78N, and a more similar c-axis thermal expansion coefficient [22]. Moreover, the compressive strain due to the growth on the ZnO underlayer promotes stabilization of an InGaN compositional phase with enhanced indium content [23, 24]. This approach also has the potential for transfer of nano InGaN-GaN structures onto alternative substrates (e.g. cheaper or flexible) through chemical liftoff via preferential etching of the ZnO underlayer [25].

In this work, we demonstrate nanoselective area growth (NSAG) as a potential route which mitigates the technological blocks resulting in high quality InGaN nanostructures on ZnO templates. ZnO template layers were grown on c-sapphire using pulsed laser deposition from a sintered 5N ZnO target in a molecular oxygen ambient with a 248 nm Krf excimer laser [26]. NSAG of InGaN was made by MOVPE through electron-beam-exposed hydrogen silsesquioxane (HSQ) masks which were fabricated using a process described in [18, 27]. Several mask formats were used, as shown in figure 1.

We first tried to pattern the HSQ directly on the ZnO without GaN on top, and then 100 nanometers of InGaN were grown. However it turned out that for MOVPE of InGaN above 730 °C ZnO starts decomposing [28]. Indeed at low growth temperature (around 730 °C), due to adsorption and lower migration of growth species on the surface of the SiO2, nucleation occurs on the exposed HSQ resulting in polycrystalline InGaN formation, leading to loss of selectivity, as seen in figure 2. Furthermore both NH3 (the standard precursor gas for atomic nitrogen N), and H2 (the standard carrier gas) back-etch the surface of the ZnO at these temperatures, which can lead to delamination of the GaN layer [29–31].

In a previous work, the authors addressed the back-etching of ZnO by growing high quality GaN by MOVPE under N2 carrier gas (normally H2) and replacing the
ammonia with 1,1dimethylhydrazine (UDMH), see [32, 33]. The use of UDMH allows for a reduction of the GaN growth temperature from the conventional range of 1000 °C–1100 °C to a range of 550 °C–800 °C (henceforth referred to as low temperature, or LT).

Hence, in an attempt to restore selectivity, 100 nm of GaN were first grown epitaxially on the ZnO at LT and then an SiO₂ overlayer mask was patterned using e-beam lithography on HSQ, see figure 1. SEM analysis shows that using this method InGaN growth at 800 °C became perfectly selective on the GaN/ZnO/Al₂O₃ samples, as seen in figure 3. Figure 4 shows that arrays of regularly-spaced InGaN nanopyramids have formed in the patterned areas. The nanopyramids exhibit aligned hexagonal faceting, and are homogenous in size, shape, and composition. The six smooth triangular semipolar (1101) facets indicate epitaxial growth. Each nanopyramid appears to be free from intrinsic defects within the detection limits of the SEM. The SEM images on figure 4 do not show any V-pit (V-pits are usually the result of propagation of threading dislocations [34, 35]). Whereas the planar InGaN in the unpatterened area exhibits 3D growth with V-pits and other defects resulting in the rough morphology quality as vividly seen from the SEM image in figure 3. As a remark we can notice evidence of micron-sized blisters in figures 3(a1) and (a4), which may be due to the underlying ZnO starting to dissociate locally, but being blocked by the GaN. The main result here is the demonstration of a novel nano-patterning process that suits fragile ZnO templates, leading to the growth of InGaN nanopyramids on LT-GaN-covered ZnO templates with perfect selectivity.

Scanning transmission electron microscopy images of the InGaN nanopyramids are displayed in figure 5. The focused ion beam lamellae were cut along the [1100] direction to account for the six-fold symmetry of the InGaN nanopyramids and hence obtain a full description of their morphology. The high-angle annular dark field images figures 5(a), (b) and (c) illustrate the monocrystallinity and the absence of threading dislocations or resulting V-defects [34, 35] within the InGaN nanopyramids. The fast Fourier transform shown in figure 5(d) confirms their wurtzite atomic arrangement. The energy-dispersive x-ray spectral maps shown in figures 5(e) and (f) highlight the homogeneity of the nanopyramids in
both indium and gallium compositions, indicating that there is a single compositional phase in the nanopyramids. Figure 5(a) also shows that the LT 100 nm thick GaN epitaxially-grown on ZnO has relatively small columnar grains, which would be expected to present many stacking faults. However the poor morphology of the LT GaN layer did not appear to affect the high quality of the InGaN nanopyramids, which were comparable with those already observed for GaN and InGaN grown on GaN-on-sapphire [18, 19] and AlN-buffered silicon [20]. Indeed, at the nanoscale, the quality of InGaN on LT-GaN-covered ZnO templates is comparably similar to that of GaN-on-sapphire or AlN-on-Si wafers thanks to our approach where the size of the opening favors formation of one crystal seed to grow regardless of the quality of substrate: as growth proceeds in the openings less than 100 nm wide diameter, the growth dynamics favor the formation of only one preferential crystal seed in the openings and all the growth in the nanopening undergoes elastic strain relaxation after reaching critical thickness without generating any strain related degradations, due to the availability of free lateral surfaces; hence we typically have no dislocations, no cracks even if the buffer layer is polycrystalline, see AlN-on-Si [20].

In addition, the optical properties of these nanostructures were studied using depth-resolved cathodoluminescence spectroscopy (CL), see figure 6. The spectra all show homogeneous main CL emission peaks in the green region of the visible spectrum, with centers between 535 nm (2.32 eV) and 519 nm (2.39 eV), respectively corresponding to relaxed high-quality In0.22Ga0.78N and In0.20Ga0.79N (calculated using [36]). There are red shifts in the emission peaks for arrays (a1), (a2) and (a3), confirming an increase in indium incorporation in these nanostructures compared to the unpatterned area. For masks (a2), (a3) and (a4), there is a distinct red-shifted shoulder which is very small, compared to the InGaN in the areas of conventional growth (a.k.a. the field, black curve on figure 6). This shows that indium incorporation is significantly more homogeneous in the nanostructures than in the field. As a remark on the red-shifted shoulders we found in a previous study [37], in the case of InGaN grown on AlN/Si substrate by NSAG, that depending on mask margin size and growth temperature, the relative and overall intensity of the two-peak emission can be controlled. The study suggests that the mask margin role in the color ratio is directly related to the delay of the transition between pseudomorphic and relaxed growth modes because of increased local TMIn concentration due to vapor phase diffusion and increased local free Indium atoms due to surface migration. The increased TMIn concentration has this effect even when it does not enhance growth rate or composition. Comparable studies by different groups have led to similar conclusions [38–40].

To conclude, NSAG of regular single-crystal InGaN nanopyramid arrays was achieved on GaN-coated ZnO epitaxial substrates by MOVPE. The relatively poor quality of the low-temperature GaN layer epitaxially grown on ZnO did not seem to impact the quality of the nanopyramids grown on top by NSAG. Indeed they were thick (100 nm), indium-rich (up to 22%), single crystalline, dislocation-free, uniform, and thus comparable to high-quality InGaN nanostructures grown on GaN (see [18, 19]) and AlN/Si (see [20]) templates. LT-GaN can also be n-doped with the ZnO templates with a high flow of silane, and optimized low temperature (800 °C) lateral growth of p-doped (precursor Cp2Mg) GaN on the InGaN nanopyramid exposed semipolar r-plane facets, coupled with the selective etching of the ZnO, has the potential to transfer the optoelectronic PIN structure onto flexible and/or cheaper substrates.

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