Journal of Alloys and Compounds 554 (2013) 258–263

Contents lists available at SciVerse ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jalcom

Properties of nanopillar structures prepared by dry etching of undoped GaN grown by maskless epitaxial overgrowth

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ARTICLE INFO

Article history:
Received 27 September 2012
Received in revised form 29 November 2012
Accepted 30 November 2012
Available online 7 December 2012

Keywords:
Maskless epitaxial lateral overgrowth
Nanopillar
Chemical treatment

ABSTRACT

Nanopillar structures were prepared by dry etching of maskless epitaxial lateral overgrowth (MELO) GaN samples using a mask of Ni nanoparticles formed upon annealing thin Ni films deposited on top of SiO_2/GaN. Under our experimental conditions the average nanopillars dimensions were close to 170 nm, with the nanopillars density close to 10^9 cm^{-2}. The nanopillars formation was random and not correlated with the threading dislocation density in MELO GaN, as evidenced by comparing the size and density of nanopillars in the wing and seed regions of MELO GaN differing in dislocation density by an order of magnitude. After dry etching the luminescent intensity of nanopillars became actually lower than the intensity from the unetched matrix due to the impact of defects introduced in the sidewalls during nanopillars formation. The intensity greatly increased, together with a decrease in the leakage current of Schottky diodes, after rapid thermal annealing of nanopillar structures at 900 °C and further increased after additional etching in KOH solution. These changes are attributed to annealing of radiation defects introduced by dry etching and further removal of the damaged region by KOH etching. The results suggest that, in nanopillar structures produced by dry etching, some increase of internal quantum efficiency alongside improvement of light extraction efficiency are responsible for the observed luminescence intensity changes.

1. Introduction

Nanopillar structures in GaN-based films, heterojunctions and GaN/InGaN multiquantum well (MQW) compositions are under intense development due to expected vast improvement of performance compared to ordinary planar structures. One of the areas where such improvements are expected is the improvement of the light extraction efficiency (LEE) and internal quantum efficiency (IQE) of GaN light emitting devices (LEDs). It is well known that, in the case of GaN, the efficiency is seriously handicapped by a relatively low LEE of LEDs and a rather high contribution of nonradiative recombination channel that limits the IQE of LEDs. The low LLE of GaN LEDs is mostly related to a low value of the angle of total internal reflection. The main contributors to nonradiative recombination in GaN LEDs seem to be localized states associated with threading dislocations (see e.g. Ref. [1]). Recently it has been demonstrated that, under optimized growth conditions in metalorganic chemical vapor deposition MOCVD or molecular beam epitaxy (MBE) techniques, GaN crystals and GaN/InGaN heterojunctions (HJs) can be prepared in the form of nanopillars (NPs), which is very advantageous for increasing the LLE values and IQE values, the latter due to the virtual absence of dislocations inside these NPs (see e.g. Refs. [2,3]). However, reproducibly growing nanopillar structures with necessary diameter, length, and density is a very technologically challenging task. An alternative approach is to grow standard planar LED structures, create on their surface a mask with multiple openings, and fabricate a nanopillar structure by dry etching (see e.g. Refs. [4,5]). The difficulty here is that the density of nanopillars should be on the order of at least 10^9 cm^{-2} to achieve reasonable total luminescence efficiency from the NPs ensemble. This is not easily done by photolithography, but can be achieved by using natural nanomasks. One of the versions of such a process employs deposition of a thin layer of Ni over a thin dielectric layer deposited on LED structure, with subsequent annealing the composition at moderate temperatures leading to Ni. The result is the breaking of the continuous Ni layer into Ni nanoparticles whose density, shape, and dimensions are regulated by the Ni layer thickness, the type and thickness of the dielectric layer, and by annealing temperature. This technique has been successfully employed by us

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http://dx.doi.org/10.1016/j.jallcom.2012.11.194

to fabricate highly efficient GaN/InGaN blue and green LEDs [6,7]. The clear downsides of this approach are the introduction of considerable radiation defects density in the nanopillar sidewalls by the dry etching process and the unresolved situation with the dislocation presence in the nanopillars themselves. In principle, there could be various scenarios at play regarding inheriting dislocations from the GaN template in this case. Case one: the process is random and the ratio of nanopillars without dislocations to the total nanopillar density is determined simply by the average area of individual nanopillar and average dislocation density. This ratio, together with the average dislocation density in the planar structure regulates the effective increase of IQE value. Case two: nanopillars are preferentially formed in the regions without dislocations. In that case the performance of nanopillar structures fabricated by dry etching would be similar to the nanopillar structures prepared by growth. Case three: nanopillars formation is favored by the presence of threading dislocations. In that case one does not expect the IQE increase for nanopillar structures prepared by dry etching. Obviously, finding out which of these scenarios is in operation is very important for judging the feasibility of the dry etch fabrication approach versus the growth approach. In what follows we try to solve this question by doing dry etching of GaN films with regions strongly differing in dislocation density. In this paper it is done by performing the process on GaN films prepared by maskless epitaxial lateral overgrowth MELO [8,9] (termed pendeo-epitaxy in the original papers). As will be shown below the dislocation density in these films varies from about 10^9 cm^{-2} in the regions of vertical growth down to about 7×10^7 cm^{-2} for the wing regions of lateral overgrowth. Our data strongly suggests that the occurrence of dislocation in the nanopillars is a random process.

The question of radiation damage introduced by dry etching is equally important. In Ref. [10] we show that this damage causes a strong increase in the leakage current of nanopillar LED structures fabricated by dry etching. It also leads to a strong dependence of the structures capacitance and leakage current on ambience and to marked persistent photoconductivity and photocapacitance of these structures [11], the effects clearly undesirable for practical LED devices. Earlier reports have shown that the detrimental effects of dry etching related radiation damage can be alleviated by subsequent etching in HCl [5], by annealing at high temperatures [10], and by annealing at high temperatures followed by additional etching in aqueous solution of KOH [10]. Detailed studies performed for undoped GaN films with nanopillar structures produced by dry etching [10] showed that the radiation defects responsible for the dry etching damage are the deep electron traps with activation energies 0.15, 0.2, 1 eV, and that finishing etching of the structures in aqua regia is very beneficial for the structures leakage current. In what follows we demonstrate that the above approaches with high temperature annealing, etching in KOH and finishing etching in aqua regia are also very efficient for nanopillar structures fabricated by dry etching on MELO GaN films and that the amount of increase in photoluminescence efficiency is higher for the high-dislocation-density regions than for low-dislocation-density regions, in reasonable agreement with simple considerations outlined above.

2. Experimental

The n-GaN templates for subsequent MELO epitaxy were grown on c-plane sapphire substrates by metalorganic chemical vapor deposition (MOCVD) (Veeco D180 GaN). Trimethylgallium and ammonia (NH_3) were used as Ga and N precursors, while silane (SiH_4) was the n-type dopant (the donor concentration in this n-type template film was 8×10^{18} cm^{-3}). Prior to growth, the sapphire substrates were heated to 1080 °C in hydrogen ambient for 6 min to remove any surface contamination. A 30-nm-thick GaN nucleation layer was deposited at 540 °C, followed by the growth of 1-μm-thick n-GaN at 1054 °C. A Ni etch mask was subsequently deposited on the n-GaN template using e-beam evaporator. A mask pattern consisting of Ni stripes of 4 μm width separated by 14 μm gaps and going in the [1–100] direction was prepared by negative photolithography and reactive ion etching. After the photoresist lift-off, the n-GaN template (thickness of 1 μm) was etched off in the gaps of the mask down to sapphire using inductively coupled plasma (ICP) dry etching. Thus, a patterned n-GaN template with 14 μm trenches and 4 μm stripes was formed for subsequent selective regrowth.

These n-GaN templates were then loaded into the MOCVD chamber for the maskless epitaxial lateral overgrowth (MELO) using the mechanism similar to pendeo epitaxy. The lateral overgrowth was achieved within the temperature range of 1050–1085 °C using the pressure of 300 torr. The thickness of this well coalesced undoped layer was close to 6 μm.

For the nanopillar fabrication, a 100 nm thick SiO_2 layer was first deposited as an interlayer on top of the prepared MELO GaN surface by plasma-enhanced chemical vapor deposition (PECVD). After the SiO_2 deposition, 5 nm thick Ni layer was deposited on the SiO_2 interlayer by e-beam evaporation. The Ni/SiO_2/GaN samples were then subjected to rapid thermal annealing (RTA) under N_2 flow at 850 °C for 1 min to form the self-assembled Ni metal clusters. Inductively coupled plasma (ICP) etching was conducted to etch the exposed SiO_2 film using the Ni nanodots as etch mask under the gas mixture of O_2 and CF_4. Then, the GaN layer was further etched down to about 0.5 μm depth by the ICP etching with Cl_2 gas. Finally, the Ni nanodots/SiO_2 remaining on the top of nanopillars were removed by a buffered oxide etchant to obtain the vertically arranged GaN nanopillars. This procedure was performed for 1 × 1 cm pieces cut from the starting MELO GaN wafer, using a part of the starting wafer not subjected to nanopillar fabrication process as a reference sample.

Following the results of our previous work on luminescence and electrical properties of nanopillar structures prepared on MOCVD n-GaN by dry etching [10] three types of postpreparation surface treatments were used for the present nanopillar MELO GaN structures: 1) as-prepared samples after reactive ion etching RIE; 2) samples after RIE and rapid thermal annealing (RTA) in N_2 atmosphere for 1 min at 900 °C; 3) samples after RIE and RTA at 900 °C and additional etching in 0.5 M KOH solution in water. In all cases respective samples were also given a final etch in cold aqua regia with rinsing in deionized water to improve electrical properties [10]. In the next sections the control MELO GaN sample is denoted as sample 1, the MELO nanopillar sample after RIE is denoted as sample 2, the RIE and RTA nanopillar MELO sample is called sample 3, and the RIE + RTA + KOH sample from the type three process is sample 4.

The cross-sectional and plan-view images of the nanopillar structure were taken using field emission scanning electron microscopy (FE-SEM, JEOL, S-4700). For electrical characterization Ni Schottky diodes of 5×10^{-3} cm^2 area were deposited on the nanopillar samples and the reference sample by vacuum evaporation through a shadow mask. An ohmic contact was done by soldering indium stripes to the unetched periphery of the nanopillar samples where the continuous GaN film was preserved. As evidenced by SEM imaging of the cleaved cross-sections of the samples, the metallic Ni film on top of nanocolumns formed a continuous layer, so that contacting the Ni Schottky diode was equivalent to contacting the nanopillars array with nanopillars connected in parallel. Electrical measurements involved taking current–voltage (*I–V*) characteristics of the Schottky diodes at various temperatures, capacitance–voltage (*C–V*) measurements at various temperatures in the dark and after illumination, admittance spectra measurements [12], and deep levels transient spectroscopy measurements (DLTS) [13]. Optical excitation in these experiments was provided by a high-power GaN light emitting diode with the peak wavelength of 365 nm. The temperature was varied in the 85–400 K temperature range. The detailed description of experimental setups can be found in our earlier papers [14,15]. Luminescence spectra of the reference sample and the nanopillar samples were measured using the microcathodoluminescence (MCL) setup described e.g. in Ref. [16]. The accelerating voltage in these experiments was 7 kV which resulted in the electron–hole pairs generation depth of about 0.4 μm, i.e. close to the thickness of the nanopillar layer.

The dislocation density in the starting MELO sample was determined by MCL imaging and electron beam induced current EBIC [17] imaging and was taken as the density of dark spot defects. The Schottky diodes used for EBIC measurements were the same as the ones used for electrical characterization. The probing beam excitation current necessary for monochromatic MCL imaging and for reliable MCL spectra measurements was rather high, on the order of some nanoampers, which resulted in considerable image blurring so that contributions from individual nanopillars could not be reliably resolved. Using panchromatic MCL imaging mode allowed to increase the optical throughput of the registration system and to apply the much lower probing beam current of 200 pA thus radically improving the spatial resolution making it possible to image individual nanopillars. (For these measurements LEO 1450 VP SEM was used). Hence, this mode was used to compare the effects of various postpreparation treatments on luminescence efficiency of nanopillars.

3. Results and discussion

3.1. Random nanopillars formation and absence of correlation with dislocation density in MELO GaN samples

The distribution of dislocation density in our MELO GaN templates was studied by means of MCL and EBIC imaging and will