Multilayer porous structures on GaN for the fabrication of Bragg reflectors

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ABSTRACT

We report on the development of electrochemical etching technology for the production of multilayer porous structures (MPS) allowing one to fabricate Bragg reflectors on the basis of GaN bulk substrates grown by Hydride Vapor Phase Epitaxy (HVPE). The formation of MPS during anodization is caused by the spatial modulation of the electrical conductivity throughout the surface and the volume of the HVPE-grown GaN substrate, which occurs according to a previously proposed model involving generation of pits and their overgrowth. We found that the topology of the porous sheets constituting the MPS is different in the vicinity of N-face and Ga-face of the bulk wafer, it being of conical shape near the N-face and of hemispherical shape near the Ga-face. The composition of electrolytes, their concentration as well as the anodization potential applied during electrochemical etching are among technological parameters optimized for designing MPS suitable for Bragg reflector applications. It is shown also that regions with various porosities can be produced in depth of the sample by changing the anodization potential during the electrochemical etching.

Keywords: GaN, Hydride Vapor Phase Epitaxy, Electrochemical Etching, Multilayer Porous Structure, Bragg Reflectors

1. INTRODUCTION

Porous semiconductors have been widely investigated since the discovery of luminescent microporous Si [1,2]. Porous silicon, exhibiting visible luminescence instead of infrared emission inherent to bulk counterpart, was viewed as a perspective material for various optoelectronic devices [3]. Later on, the field for applications of porous silicon was broadened towards biomedical and sensor applications [4], due to unique properties of this biodegradable material [5]. At the same time, porous structures of other semiconductors started to attract a lot of interest, especially those of porous III-V and II-VI semiconductors. Possibilities for efficient phonon engineering by porosification have been demonstrated in GaP, GaAs and InP [6-11]. A strongly enhanced optical SHG and THz emission were observed and studied in porous GaP and InP membranes [12-15]. Porous matrices were found to contribute to the formation of superior electrical and emission characteristics of novel polymer-semiconductor nanocomposites promising for display applications [16]. The occurrence of self-arrangement of submicrometer pores in two-dimensional hexagonal lattice observed in anodically-etched GaP and InP, especially the non-lithographic growth of 2D single crystals of nanopores with lattice constant as small as 100 nm as a result of electrochemical dissolution of InP [17], and preparation of 3D microstructures by self-induced voltage oscillations during anodic etching of n-InP [18], along with technologies developed for metalizing porous templates open large opportunities for electronic and photonic applications [19-21]. Fabrication of porous structures with controlled porosity has also been demonstrated in wider bandgap II-VI compounds such as ZnSe and CdSe [22-24]. Particularly, porosity-induced gain of luminescence was observed in strongly light scattering CdSe porous medium [25].

At the same time, less attention has been paid to the preparation of porous GaN, basically due to the high density of threading dislocations inherent to the material. Earlier investigations demonstrated that photoelectrochemical etching of GaN results mainly in the fabrication of nanowires or pyramidal structures genetically bound to threading dislocations

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[26,27]. The development of the metal organic chemical vapor phase deposition (MOCVD) for the growth of GaN, and the production of the material with better quality opened possibilities for the control of porosity by electrochemical etching followed by thermal annealing. It was demonstrated that the porosity of MOCVD-grown GaN can be controlled by both the anodic voltage and sample doping [28,29], while annealing leads to a shape transformation in nanoporous GaN, which opens possibilities to produce buried cavities and nanomembranes [30,31]. Since electrochemical porosification is an effective way to control the index of refraction of GaN [32], it was proposed to prepare multilayer porous structures in GaN using electrochemical etching [33], which is of crucial importance for optical engineering of GaN, particularly when designing lasers, microcavities and distributed Bragg reflectors (DBRs). The applicability of multilayer porous structures based on MOCVD-grown GaN for the design of DBRs has been recently demonstrated [33].

The prospects for the preparation of porous structures in hydride vapor phase epitaxy (HVPE) grown GaN remains even less explored, in spite of the fact that HVPE has been identified during the last decade as one of the most relevant techniques for the growth of bulk GaN for substrates needed for further progress in the development of III-nitride-based power electronics and high brightness light emitting devices. HVPE ensures the highest growth rates (up to 500 μm per hour) and favors the growth of thick GaN layers which are subsequently detached from the sapphire or other foreign substrates. However, the quality of the produced material still requires substantial improvement. Particularly, it was observed that the HVPE-grown GaN is usually non-uniform due to peculiarities of the growth process, which is governed by the formation and subsequent overgrowth of the so-called V-type defects or pits on the film surface [34].

The goal of this paper is to investigate the impact of the electrochemical etching conditions upon the morphology of the obtained porous structures in HVPE-grown GaN for their applications as Bragg reflector.

2. EXPERIMENTAL

The HVPE-grown samples used in experiments were acquired from SAINT-GOBAIN Crystals. They represent 2-inch diameter 300-μm thick wurtzite-phase *n*-GaN single crystalline templates of (0001)-orientation with the density of threading dislocations in the range $(1–2)\times10^7$ cm^{-2}.

The as-grown structures were subjected to electrochemical etching to produce porous structures. Electrochemical etching was carried out in HNO_3, or HCl aqueous electrolytes at room temperature in a common two electrode cell where the sample served as working electrode. A platinum wire (0.5-mm diameter) mesh with the surface of 6 cm^2 was used as counter electrode. An anodic voltage was applied to the sample, magnetic stirring being used to maintain the homogeneity of the electrolyte during electrochemical etching. A Keithley's Series 2400 Source Measure Unit was used as potentiostat.

The morphology of electrochemically etched GaN samples was studied using Zeiss Ultra Plus and VEGA TESCAN TS 5130MM scanning electron microscopes.

3. RESULTS AND DISCUSSION

It was shown in a recent study that the HVPE-grown GaN material is inhomogeneous both on the surface and in the bulk, as found by SEM, atomic force microscopy (AFM) and Kelvin Probe Force Microscopy (KPFM) investigations [34]. Figure 1 illustrates the morphology of an electrochemically etched GaN sample after removal of the surface layer.

Well-defined circular regions comprising concentric topographical ring-like structures, sometimes with quasi-hexagonal shape, are observed in the image from Fig. 1. The width of ring-like features was estimated to be of the order of 80–150 nm. Since the electrochemical etching techniques are highly sensitive to local doping, it was suggested that this topology is due to the spatial modulation of the electrical conductivity throughout the surface and the volume of the HVPE-grown GaN wafer, the most probable source for these modulations being the difference in the background doping concentrations in the bright and dark areas for the ring-like structures observed. This hypothesis was confirmed by a combined AFM, KPFM, SEM and micro-CL study [34].