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B. Damilano, S. Vézian, J. Massies. Photoluminescence properties of porous GaN and (Ga,In)N/GaN single quantum well made by selective area sublimation. *Optics Express*, 2017, 25 (26), pp.33243. 10.1364/oe.25.033243 . hal-03553879

**HAL Id: hal-03553879**

**<https://hal.science/hal-03553879>**

Submitted on 3 Feb 2022

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# Photoluminescence properties of porous GaN and (Ga,In)N/GaN single quantum well made by selective area sublimation

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**Abstract:** Porous GaN and (Ga,In)N/GaN single quantum well layers are fabricated using a selective area sublimation (SAS) technique from initially smooth and compact 2-dimensional (D) layers grown on Si(111) or c-plane sapphire substrates. The photoluminescence properties of these porous layers are measured and compared to reference non-porous samples. Whatever the substrate used, the porosity leads to an increase of the room temperature photoluminescence intensity. The magnitude of this increase is related to the initial defect density of the 2D epitaxial layers and to the degree of carrier localization prior to the SAS process.

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**OCIS codes:** (160.4236) Nanomaterials; (250.5230) Photoluminescence; (160.2540) Fluorescent and luminescent materials.

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## 1. Introduction

For over a decade now, porous GaN is the subject of continuous research interest because of a wide range of potential applications including high-sensitivity sensors [1], water splitting for renewable hydrogen production [2], energy storage [3,4], GaN separation and layer transfer [5], and optical devices such as light-emitting diodes (LEDs) [6,7]. Also, the refractive index variation as a function of the porosity has been exploited for the fabrication of high-reflectivity and low-strained GaN-based distributed Bragg reflector and for light confinement in edge-emitting laser diodes [8,9]. Furthermore, it is used as template for epitaxial overgrowth of compact GaN and In<sub>x</sub>Ga<sub>1-x</sub>N epitaxial layers with both strain and dislocation density reduction and finally improved performance of LEDs [10,11]. These results have mainly motivated the present work. Actually, we have recently shown that using selective area sublimation (SAS), GaN nanowires including In<sub>x</sub>Ga<sub>1-x</sub>N quantum disks can be easily fabricated from standard 2-dimensional (D) epitaxial layers [12,13]. However, for almost all the applications cited above, porous GaN based materials present an obvious advantage over nanowires for device applications which is the larger active material density generally obtained. Within this context, the aim of this paper is to report a comparison of the photoluminescence properties of 2D GaN and In<sub>x</sub>Ga<sub>1-x</sub>N epitaxial layers before and after transforming to porous by SAS. In particular, we focus here on the porosity effect on thin epitaxial layers of GaN on Si. Indeed, a simple process for obtaining high luminescence

efficiency for such highly defective layers still needs to be developed to fully exploit the possibilities of GaN-based device integration on Si.

## 2. Experimental

The structures of the samples studied in this work are schematized in Fig. 1. Three different samples are used for the fabrication of porous layers. Sample A and B are grown by molecular beam epitaxy (MBE) using  $\text{NH}_3$  as the nitrogen source and solid sources for the other elements (Ga, Al, In, Si) on a Si(111) substrate. The structure is initiated by 100 nm of AlN followed by a 250-nm thick GaN layer. The threading dislocation density emerging at the surface is  $3 \times 10^{10} \text{ cm}^{-2}$  according to transmission electron microscopy and X-ray diffraction experiments. The structure of sample B is identical to sample A excepted that a 2 nm-thick (Ga, In)N quantum well and a 30 nm GaN barrier layer are added on the top of the structure. Sample C is grown by metal organic chemical vapor deposition (MOCVD) and is a 2.5  $\mu\text{m}$ -thick GaN layer grown on sapphire (0001) substrate. The dislocation density is  $5 \times 10^8 \text{ cm}^{-2}$  according to atomic force microscopy experiments [14]. For sample p-C, an  $\text{Al}_{0.2}\text{Ga}_{0.8}\text{N}$  (20 nm) etch-stop layer and a 250-nm thick GaN layer are grown by MBE on top of sample C.

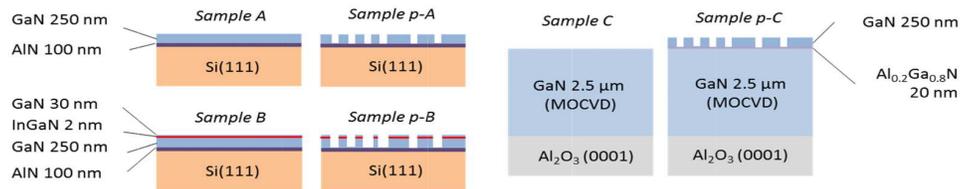


Fig. 1. Structure of the samples.

These planar samples (A,B,C) are transformed in porous layers (p-A, p-B, p-C) by using an *in situ* deposited  $\text{Si}_x\text{N}_y$  nanomask and a SAS method [12,13]. In the MBE chamber, the surface of the samples is exposed to a Si flux for 15 minutes (the Si cell temperature is  $1220^\circ\text{C}$ ) leading to the formation of an uncomplete  $\text{Si}_x\text{N}_y$  monolayer (or  $\text{SiGa}_3\text{N}_3$  according to Markurt et al. [15]). Then the samples are heated at a temperature of  $900^\circ\text{C}$  under vacuum for 25 min. This induces the sublimation of the GaN in the regions left unprotected by the  $\text{Si}_x\text{N}_y$  nanomask. This SAS process results in the formation of pores with a mean perimeter of 59 nm, 52 nm, and 65 nm for samples p-A, p-B, and p-C, respectively, as measured from plan-view scanning electron microscopy (SEM) images of Fig. 2. The surface occupied by the pores corresponds to 0.38, 0.30 and 0.27 of the total surface for samples p-A, p-B and p-C, respectively. The pores extend almost down to the AlN or the  $\text{Al}_{0.2}\text{Ga}_{0.8}\text{N}$  layer, meaning that the pore depth (perpendicular to the surface) is  $\sim 250 \text{ nm}$  as shown in Fig. 2.

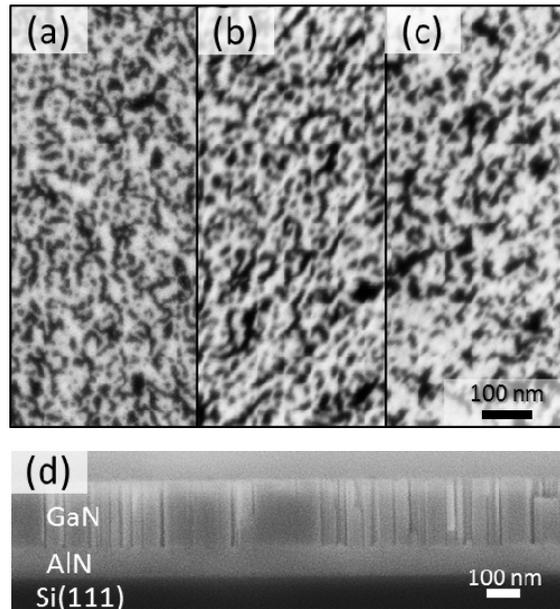


Fig. 2. Scanning electron microscopy in plane-views of samples p-A (a), p-B (b), and p-C (c). Cross-section image of sample p-B (d).

The optical properties of these samples are studied using CW photoluminescence (PL). The laser source is a frequency-doubled Ar laser at 244 nm with an excitation power of 20 mW. The samples are all measured in the same PL run, side by side, and therefore the PL intensities are directly comparable. 95% of the laser light is absorbed in the top 100 nm of GaN.

### 3. Results and discussions

We first discuss the PL energy variations observed between porous and non-porous samples grown on Si(111) substrate. The room-temperature PL spectra of samples A and p-A are shown in Fig. 3(a). The PL spectrum of sample A is dominated by a band at 3.407 eV corresponding to the emission of A free excitons of GaN in a quasi-strain free state [16,17]. The PL spectrum of sample p-A is dominated by a peak at 3.424 eV. Making porous GaN leads to the formation of free edges which are efficient to relax eventual stresses in the material. Therefore, the 17 meV shift towards higher energies between samples A and p-A is probably not due to a change in the GaN stress state from relaxed to compressive, but rather to dielectric confinement as explained by Zettler et al. in the case of thin nanowires [18]. Note that the ratio of the GaN 0-phonon band and LO-replica indicates a different doping level [19]. The (Ga,In)N/GaN QW from sample C emits in the blue at 2.67 eV, while for the porous sample p-B the emission energy is shifted to 2.75 eV (Fig. 3(b)). Initially, the (Ga,In)N QW of sample B is in biaxial stress (compressive) in the GaN matrix. Due to the porosity, this stress can be relaxed (at least partially) at the free edges of the pores. A change from a compressive to a more relaxed stress state should induce a red-shift of the PL energy which is clearly not what we observe here. Actually, we have to remind that a strong electric field is present in the quantum well due to the difference of piezoelectric and spontaneous polarizations with the barriers [20–22]. If the compressive stress state decreases, then the resulting piezoelectric field in the (Ga,In)N quantum well also decreases. Therefore the quantum confined Stark effect is less pronounced and can explain the observed blue-shift of the QW PL peak [23]. The PL full width at half maximum of the (Ga,In)N QW is respectively

166 meV and 145 meV for the non-porous sample B and the porous sample p-B. This reduction of the FWHM can be also related to the decrease of the internal electric field.

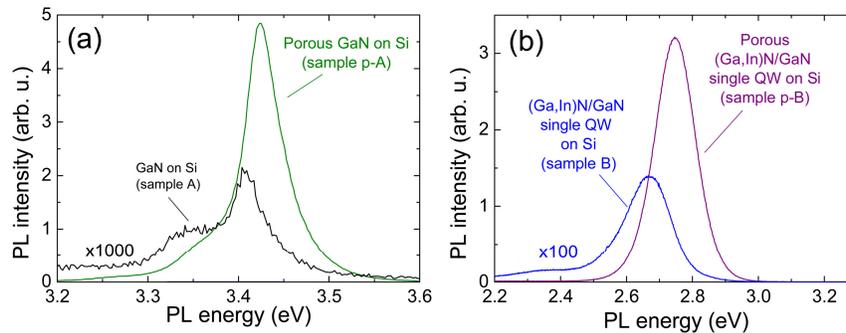


Fig. 3. Room temperature photoluminescence spectra of samples A, p-A, B and p-B.

The salient feature in the spectra shown in Fig. 3 is the strong PL intensity improvement of the porous samples compared to the non-porous ones: the room temperature PL intensity of samples p-A and p-B are respectively  $>2000$  and  $>200$  times stronger than samples A and B. This large PL intensity increase first shows that the non-radiative surface recombination velocity at the pore edges is weak, indicating that the pore sides are not damaged by the thermal treatment, as it can be the case when high-energy plasmas are used to etch GaN. Furthermore, this means that part of the dislocations have been etched away during the sublimation process [24] and / or efficient carrier localization processes take place similarly to the case of GaN quantum dots [25, 26]. Indeed, samples A and B are very thin layers grown on Si(111) substrates and are affected by a large density of dislocations ( $3 \times 10^{10} \text{ cm}^{-2}$ ) and therefore the PL intensity is critically degraded by these defects [27]. Note that if the sample A is covered by a thicker  $\text{Si}_x\text{N}_y$  layer (exposition of the GaN surface to the Si flux for 75 min. instead of 15 min.) and annealed with the same conditions than for p-A, a 2D surface without pits and no improvement in the PL yield compared to sample A are observed. This shows that the annealing procedure in itself is not responsible of the PL intensity increase. We can postulate that by using a less defective material, the PL intensity increase after making porous the epitaxial 2D structure should be smaller. To check this hypothesis we have measured the PL characteristics of sample p-C, a porous GaN layer made from a lower dislocation density ( $5 \times 10^8 \text{ cm}^{-2}$ ) GaN layer grown on sapphire by MOCVD. The corresponding PL spectra are shown in Fig. 4(a). The PL intensity of sample p-C is 3 times larger than sample C. As expected, this ratio is much smaller than in the case of porous GaN on Si. This relatively small PL intensity increase can be due to a larger extraction efficiency factor for the porous sample. It is interesting to point out that the PL intensity of sample p-A is only 2.2 times smaller than sample p-C (Fig. 4(b)), while the initial dislocation density in the 2D material of sample A was 60 times larger than for sample C. This shows that by using nanoporous GaN instead of 2D compact layers, the photoluminescence efficiency of a very thin GaN layer ( $<0.3 \mu\text{m}$ ) on Si can be close to that of a thick GaN layer ( $> 2 \mu\text{m}$ ) on sapphire.

The porous (Ga,In)N/GaN quantum well (p-B) gains a factor  $>200$  compared to sample B, *i.e.* a factor 10 times lower than for the pure GaN sample (p-A). The difference in these factors can be explained by the fact that excitons can be localized in potential minima of the (Ga,In)N quantum well (due to In composition fluctuations or QW thickness fluctuations) [28]. Due to this localization effect, the excitons are less sensitive to diffusion to defects. This explains the smaller PL intensity increase factor for the sample p-B.

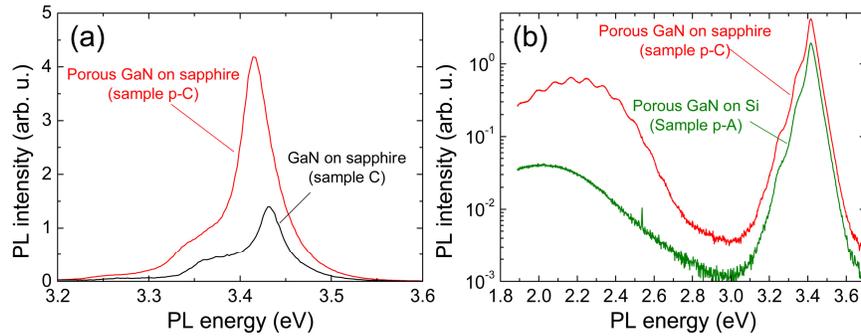


Fig. 4. (a) Room temperature photoluminescence of samples C and p-C. (b) Comparison of the room temperature photoluminescence of sample p-A and p-C (log. scale).

Finally we have measured the temperature dependence of the porous (Ga,In)N/GaN quantum well (p-B) in order to evaluate the room temperature efficiency of this sample and therefore the potential of porous (Ga,In)N quantum wells as the active zone of optical devices. The PL spectra and the Arrhenius plot of the integrated PL intensity of the (Ga,In)N quantum well are shown in Fig. 5. The PL intensity ratio between low and room temperature is 9.5, which is relatively small according to the very large dislocation density of the initial non porous sample. The non-radiative channel responsible of the intensity decrease corresponds to an activation energy of 46 meV. This can be interpreted as the carrier escape from localized states [29] or exciton dissociation [30].

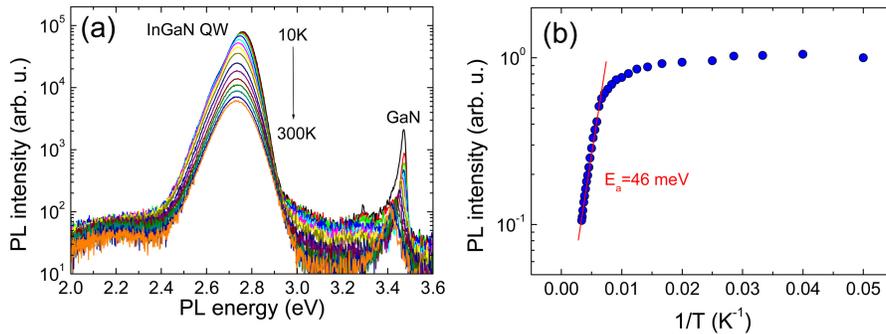


Fig. 5. (a) Temperature dependence of the photoluminescence spectra of sample p-B. (b) Arrhenius plot of the integrated photoluminescence intensity of the (Ga,In)N quantum well of sample p-B. A non-radiative process corresponding to an activation energy of 46 meV is found.

#### 4. Conclusion

It is shown that transforming GaN-based standard epitaxial layers in porous material by a simple process of selective area sublimation (SAS) systematically leads to an increase of the room-temperature photoluminescence intensity. An increase up to 3 decades is obtained when the initial dislocation density is high and much less pronounced for an initial low dislocation density material. Therefore, this process is of specific interest for structures affected by a large density of defects, such as very thin layers grown on Si substrate. The case of very thin GaN layers including  $\text{In}_x\text{Ga}_{1-x}\text{N}$  quantum wells is of prime interest to get visible emission devices integrated to the Si based microelectronic platform, however the thermal budget imposed by the sublimation process can be a serious limitation which has to be taken into account to avoid the degradation of CMOS performances.

**Acknowledgments**

The authors would like to thank M. Leroux for helpful advice and support on photoluminescence experiments, E. Frayssinet for providing the GaN MOCVD template.