

GaN ultrathin membrane for SERS detection of Rhodamine B

V. Ciobanu¹, I. Plesco¹, T. Braniste¹, G. Ceccone², P. Colpo², I. Tiginyanu¹

¹ National Center for Materials Study and Testing, Technical University of Moldova, Stefan cel Mare av. 168, Chisinau 2004, Moldova

² Joint Research Center, European Commission, via E. Fermi 2749, 21027 Ispra, Italy

Abstract— In this paper we demonstrate the fabrication of a SERS detector based on GaN ultrathin membrane. The GaN membranes are elaborated by the so-called Surface Charge Lithography approach. The obtained membranes are functionalized by 20 nm Au nanodots and characterized by different tools in order to demonstrate the material quality and sensitivity enhancement for Rhodamine B detection in the micromolar range.

Keywords— GaN membrane, SERS detector, Rhodamine B sensor, Surface Charge Lithography, Au nanodots.

I. INTRODUCTION

Optical sensors and biosensors represent an easiest way to detect a very low concentration of specific molecules. There are different types of these kind of optical sensors, but most of them includes very sophisticated and expensive tools. However, the combination of Surface Plasmon Resonance with a Raman Scattering effect proved to be very efficient for the determination of even nM concentration of biogenic amines [1]. Paper based SERS (Surface Enhanced Raman Scattering) sensor [2] which consists of Au nanoparticles deposited on paper substrate proved to be as efficient as solid substrates like quartz, glass or others, but these kinds of sensors are single use ones and not stable in some hazardous solutions compared to GaN substrate which is a very chemically stable material.

GaN is nowadays considered as the second most important semiconductor after Si and it has a wide range of applications like high power electronics [3], high frequency devices [4], biosensors [5], optoelectronics [6], pressure sensors [7], battery energy storage systems [8], memristive systems [9] etc. The nanostructured GaN could enhance some specific properties of the material due to its enhanced surface area as it was previously demonstrated for concrete applications like hydrogen production [10].

Rhodamine B (Rh B) is a widely used dye in the industry like dyeing in textile, leathers, printing and so on. The organic dyes can however cause serious problems for environment or biodiversity. Moreover, the presence of Rh B was reported also in food industry, as it was found in chili powder, sausage, sweets, preserved plums. As Rh B is considered as potentially carcinogenic [11], it's use in food industry should be strictly controlled by law. Thus, the low

concentration and a fast way for the detection of these molecules in food or in the residual water is a very important task.

II. RESULTS AND DISCUSSION

A. Fabrication of GaN membranes

For the fabrication of GaN ultrathin membranes, the so-called surface charge lithography approach was used, a technique developed previously at the National Center for Material Study and Testing [12]. A commercial unintentionally doped MOCVD (metal-organic chemical vapor deposition) grown GaN wafer with the concentration of free carriers of $5 \cdot 10^{-17}$ was used. A traditional photolithographic process was done in order to have the desired pattern of the membranes. After the developing process, the membrane is subjected to Ar⁺ plasma treatment. The plasma conditions are very well defined and controlled. The ion dose was maintained at 10^{11} ions/cm² in order to have a penetration depth of the ions up to 15 nm in the material according to the previous Monte Carlo simulations [13]. In the last lithographic step, the remained photoresist is dissolved in acetone. The process is followed by a photoelectrochemical etching in a low concentrated KOH solution under UV light illumination. The electrical closed circuit is maintained at 0 V and the current value is continuously monitored by using a Keithley instrument. The fabrication process of the ultrathin GaN membranes is illustrated in the figure below.

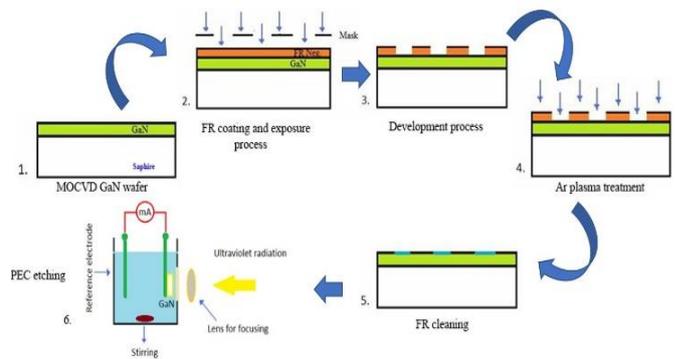


Fig. 1 Fabrication steps of the GaN membranes

B. SEM and TEM analysis of the membranes

The morphology of the membranes (figure 2a, b) was studied by scanning electron microscopy (SEM) Zeiss Gemini Ultra55 Plus working at 10 kV and transmission electron microscopy (TEM) investigations were carried out with FEI Tecnai F30 G2 STwin equipment operated at 300 kV (field emission gun, spherical aberration coefficient CS = 1.2 mm).

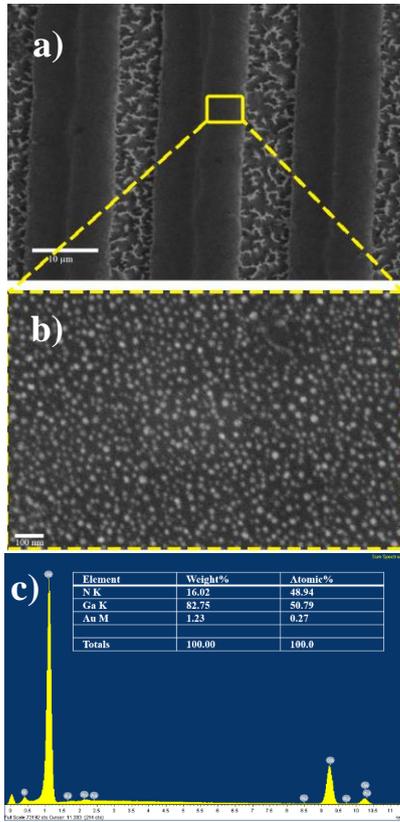


Fig. 2 SEM images of (a) GaN membranes, (b) membrane functionalized with Au dots and (c) EDX analysis

The EDX (energy dispersive X-ray) analysis shown in figure 2c clearly demonstrates the presence of Au on top of the thin membrane.

A thin GaN membrane transparent to e-beam is imaged in figure 3a. The high resolution (HR) micrograph figure 3b reveals single crystalline texture of membrane. The fast Fourier transformation (FFT) in figure 3c was taken from the full region in b and demonstrates wurtzite type $P6_3mc$ GaN structure oriented along [0001] zone axis. At the same time no additional reflections were observed. The FFT matches perfectly to simulated diffraction pattern on figure 3d.

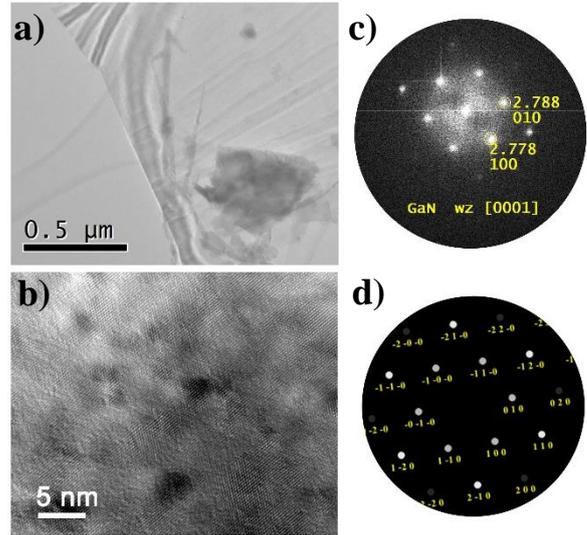


Fig. 3 Crystallographic analysis of GaN nanomembrane: (a) an overview TEM micrograph, (b) HR micrograph, (c) FFT collected from (b), (d) simulated diffraction pattern of wurtzite GaN oriented along [0001] axis.

C. XPS analysis

The surface chemistry was assessed by X-Ray Photoemission Spectroscopy (XPS). XPS analysis was carried out by means of an Axis Ultra-DLD spectrometer equipped with a non-monochromatic Mg $K\alpha$ source ($h\nu = 1253.6$ eV). The take-off angle (ToA) respect to the sample normal was 0° for survey and high-resolution (HR) spectra. Surface charging was compensated using low energy (~ 4 eV) electrons and adjusted using the charge balance plate on the instrument. Selected samples were also analyzed after ion cleaning. The spectra were calibrated setting hydrocarbon C 1s at 285.0 eV.

Figure 4a shows the survey spectra of the GaN wafer surface. It shows the presence of almost stoichiometric gallium and nitrogen species, carbon due to contamination in air, but also oxygen species which according to the high-resolution analysis of Ga photoemission peaks, a shift to higher binding energy of about 0.5 eV is observed, being attributed to a thin native oxide layer (figure 4c).

In case of the GaN membrane after Ar etching for 5 min (figure 4b), a higher content of oxygen species was detected. The nitrogen content decreases because the Ar etching causes a preferential etching of nitrogen in GaN thus resulting in formation of metallic gallium.

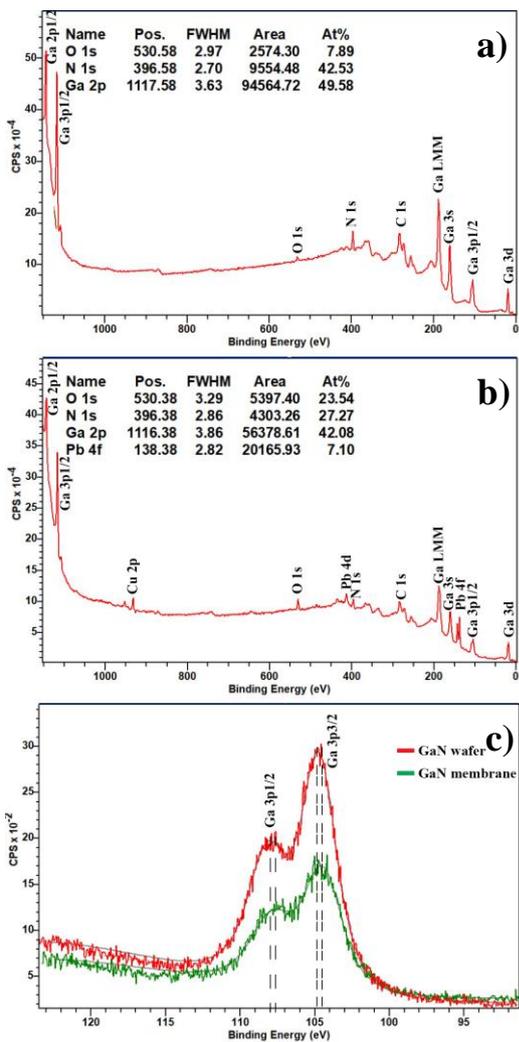


Fig. 4 XPS spectra of: (a) GaN wafer; (b) GaN membrane and (c) a comparison on the position of Ga 3p photoemission peak in case of GaN wafer and GaN membrane

Even if the oxygen concentration was found higher than in case of GaN wafer, all the Ga photoemission peaks are shifted to lower binding energies suggesting the non-oxidative state. About 7% of Pb and Cu species were additionally found which are attributed to the contamination from silver paste which was used in the photoelectrochemical process for contacting electrically the GaN surface with the electrode.

D. Raman and SERS measurements

The Raman instrument used for measurements was an inVia Renishaw equipped with a confocal microscope. The spectra were collected using the 532 nm laser and 100x

objective lens with aperture NA = 0.80 for focusing the light on the sample surface. The Raman spectra of a ultrathin GaN membrane is presented in figure 5a. The main peak at 568.2 cm^{-1} which is attributed to E2(high) Raman active mode is redshifted with about 0.6 cm^{-1} compared to theoretical study of the GaN vibrational modes. This redshift is attributed to the dislocations and stress induced into the material during the MOCVD growth process on sapphire substrate.

For the functionalization of GaN membrane, a 5 nm Au layer was deposited using a Cressington 108 Sputter Coating System. The formed Au layer is transformed into Au nanodots after a thermal treatment of the sample at 300 $^{\circ}\text{C}$ for 1 h (as shown in figure 2b).

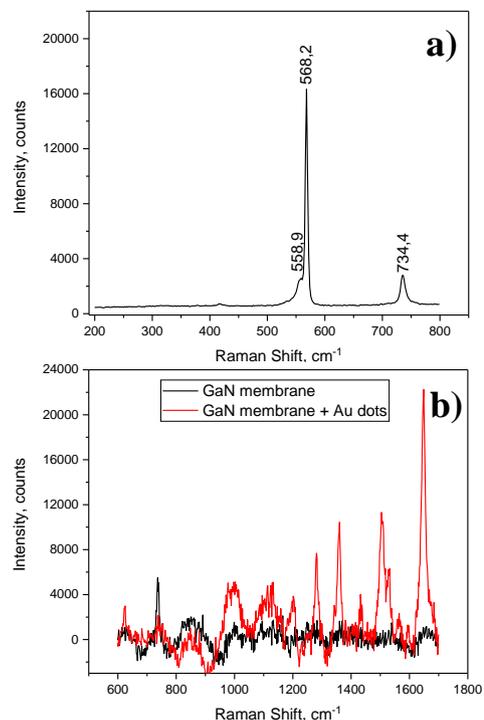


Fig. 5 (a) Raman spectrum of GaN ultrathin membrane and (b) SERS signal for detection of Rhodamine B on a as grown GaN membrane and on a Au dots functionalized membrane

The aqueous solution consisted of 1 μm Rhodamine B dissolved in deionized water (Millipore, MilliQ System). The samples were deepened into the Rh B containing solution for 10 min and then let dry in air at room temperature before Raman measurements. The Raman characterization was performed on 10 different locations on the sample surface and the average result after baseline subtraction is represented in figure 5b.

The Raman band located at 619 cm^{-1} is attributed to the xanthene ring puckering mode. The most intense bands in the region from 1100 to 1700 cm^{-1} on the Raman spectrum of Rh B were related to C–C, C–H and C=C [14]. A detailed assignment of the vibrational peaks is given in Table 1. In figure 4, characteristic peaks at 1360 cm^{-1} , 1504 cm^{-1} , and 1648 cm^{-1} are relatively obvious on SERS spectra of Rh B aqueous solutions. For the quantitative analysis, the peak located at 1648 cm^{-1} is best suited for the assessment of Rh B and was selected for characterization. As can be seen, a Raman scattering enhancement factor of about 20 in case of sample functionalized with Au nanodots was found. The SERS effect is attributed to the excitation of the Surface Plasmons which causes an enhanced local electromagnetic field around the Au nanodots.

Table 1 Rhodamine B Raman peaks positions

Peak position, cm^{-1}	Assignment
620	Xanthene ring puckering
1200	C–C bridge band stretching and aromatic C–
1281	H bending
1360	Aromatic C–C bending
1504	Aromatic C–H bending
1527	
1648	Aromatic C–C bending and C=C stretching

III. CONCLUSIONS

In this work, we demonstrate the fabrication of ultrathin GaN membranes with single crystalline structure which after functionalization by Au dots prove to be efficient as SERS sensor for the detection of micromolar quantity of Rhodamine D molecules. The enhancement factor compared to non-functionalized samples was about 20.

ACKNOWLEDGMENT

The authors acknowledge the financial support from European Commission under the Grant #810652 “Nano-MedTwin” and from the Ministry of Education, Culture and Research of the Republic of Moldova under the Grant #20.80009.50007.20.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

REFERENCES

- Buccolieri A, Bettini S, Salvatore L et al. (2018). Sub-nanomolar detection of biogenic amines by SERS effect induced by hairy Janus silver nanoparticles. *Sensors and Actuators B: Chemical*. 267:265–71. <https://doi.org/10.1016/j.snb.2018.04.028>
- Lin S, Hasi W-L-J, Lin X et al. (2015). Rapid and sensitive SERS method for determination of Rhodamine B in chili powder with paper-based substrates. *Anal Methods*. 7(12):5289–94. <https://doi.org/10.1039/C5AY00028A>
- Li H, Li X, Zhang Z et al. (2016). Design consideration of high power GaN inverter. In: 2016 IEEE 4th Workshop on Wide Bandgap Power Devices and Applications (WIPDA). 2016. p. 23–9.
- Palacios T, Mishra UK (2011). 5.06 - GaN-Based Transistors for High-Frequency Applications. In: Bhattacharya P, Fornari R, Kamimura H, editors. *Comprehensive Semiconductor Science and Technology*. Amsterdam: Elsevier; 2011. p. 242–98. <https://doi.org/10.1016/B978-0-44-453153-7.00021-3>
- Tai T-Y, Sinha A, Sarangadharan I et al. (2019). Design and Demonstration of Tunable Amplified Sensitivity of AlGaIn/GaN High Electron Mobility Transistor (HEMT)-Based Biosensors in Human Serum. *Analytical Chemistry*. 91(9):5953–60. <https://doi.org/10.1021/acs.analchem.9b00353>
- Dylewicz R, Patela SZ, Paszkiewicz R (2004). Applications of GaN-based materials in modern optoelectronics. In: Romaniuk RS, editor. *Photonics Applications in Astronomy, Communications, Industry, and High-Energy Physics Experiments II*. SPIE; 2004. p. 328–35.
- Dragoman M, Ciobanu V, Shree S et al. (2019). Sensing up to 40 atm Using Pressure-Sensitive Aero-GaN. *physica status solidi (RRL) – Rapid Research Letters*. 13(6):1900012. <https://doi.org/10.1002/pssr.201900012>
- Moradpour M, Ghani P, Gatto G (2019). A GaN-Based Battery Energy Storage System for Residential Application. In: 2019 International Conference on Clean Electrical Power (ICCEP). 2019. p. 427–32.
- Dragoman M, Tiginyanu I, Dragoman D et al. (2018). Learning mechanisms in memristor networks based on GaN nanomembranes. *Journal of Applied Physics*. 124(15):152110. <https://doi.org/10.1063/1.5034765>
- Zhang M, Zhao S, Zhao Z et al. (2021). Piezocatalytic Effect Induced Hydrogen Production from Water over Non-noble Metal Ni Deposited Ultralong GaN Nanowires. *ACS Applied Materials & Interfaces*. 13(9):10916–24. <https://doi.org/10.1021/acsami.0c21976>
- Nestmann ER, Douglas GR, Matula TI et al. (1979). Mutagenic activity of rhodamine dyes and their impurities as detected by mutation induction in Salmonella and DNA damage in Chinese hamster ovary cells. *Cancer research*. 39(11):4412–7.
- Volciuc O, Braniste T, Sergentu V et al. (2015). Fabrication of photonic crystal circuits based on GaN ultrathin membranes by maskless lithography. In: Tiginyanu IM, editor. *Nanotechnology VII*. SPIE; 2015. p. 8–17.
- Stevens-Kalceff MA, Tiginyanu IM, Popa V et al. (2013). Cathodoluminescence characterization of suspended GaN nanomembranes. *Journal of Applied Physics*. 114(4):43516. <https://doi.org/10.1063/1.4816562>
- Wang Y, Chen H, Dong S et al. (2006). Surface-enhanced Raman scattering of silver-gold bimetallic nanostructures with hollow interiors. *The Journal of Chemical Physics*. 125(4):44710. <https://doi.org/10.1063/1.2216694>

Author: Vladimir Ciobanu
 Institute: Technical University of Moldova
 Street: 168, Stefan cel Mare av.
 City: Chisinau
 Country: Moldova
 Email: vladimir.ciobanu@cstm.utm.md