Light-emitting p-i-n GaP/GaPAs NW encapsulated in a flexible PDMS membrane

S M Mukhangali¹, V Neplokh¹, F M Kochetkov¹, E I Moiseev¹, A S Miroshnichenko¹, K B Deriabin⁴, A G Nasibulin³, R M Islamova⁴ and I S Mukhin¹,⁴

¹ Saint Petersburg Academic University, 8/3 Khlopina, St. Petersburg 194021, Russia
² Peter the Great St. Petersburg Polytechnic University, 29 Politekhnicheskaya, St. Petersburg 195251, Russia
³ Skolkovo Institute of Science and Technology, 30 Bolshoy Boulevard, bld. 1, Moscow 121205, Russia
⁴ Saint Petersburg State University, 7/9 Universitetskaya Emb., St Petersburg 199034, Russia

E-mail: sungat15004@gmail.com

Abstract. Our work is aimed at the method of fabricating arrays of semiconductor III-V NWs transferred into a flexible polymer membrane made of polydimethylsiloxane. GaP / GaPAs NWs with an axial p-i-n structure were synthesized by molecular beam epitaxy. The synthesized NW arrays on substrates were encapsulated into a silicone membrane by the G-coating method in a swinging-bucket centrifuge. After membranes were treated in a plasma mixture of O₂ / CF₂ gases to open the NWs tops, which ensured the application of conductive transparent contacts - single-walled carbon nanotubes obtained by aerosol chemical method. At the last technological stage, the membranes were separated from substrates by peeling with a razor blade and the second carbon nanotubes contact was formed. The obtained LED NW/silicone membranes were characterized by I-V and the electroluminescence spectroscopy measurements.

1. Introduction
The demand for flexible optoelectronics is growing every year. Flexible devices such as displays for TV and smartphones are more often based on organic light-emitting diodes (OLEDs), which have relatively high brightness and low manufacture cost. However, OLEDs have a low quantum efficiency (EQE 2-30%), luminescence (about 10²-10⁴ cd / m²), and a limited lifespan [1,2]. Inorganic LEDs based on thin-film technology have superior device properties, but thin-film LED transfer to a flexible carrier is highly complicated since it requires laborious operations of etching, structuring, and separation from the growth substrate. An alternative provided by inorganic nanowire (NW) arrays embedded into flexible polymer is a promising solution to this problem because it combines the efficiency of inorganic materials and the simplicity of manufacturing flexible devices [3]. Moreover, such applications as augmented reality (AR), interior displays for vehicles and wristband requires LEDs with high brightness that can be achieved from NWs encapsulated into flexible polymer [4].
2. Fabrication

GaP NWs were synthesized by vapor-liquid-crystal mechanism on silicon (111) substrates in a molecular beam epitaxy setup. The silicon substrates were processed to form a SiO₂ mask layer for subsequent deposition of Ga material, forming droplets for self-catalyzed NW synthesis [5]. NWs have an axial p-i-n structure with a direct bandgap insertion of GaPAs. The p-region is doped with Be atoms, and the n-region is doped with Si. The density of the NWs was estimated to be 0.11 NWs per 1 μm².

The encapsulation of GaP/GaPAs NWs in a silicon polymer was performed by the G-coating method [3] that results in a perfect distribution of viscous polydimethylsiloxane pre-polymer gel between NWs of a dense array due to the centrifugal force direction along the wires. This method preserves the verticality of nanowires, provides complete encapsulation of the NW array and the required thickness of silicone film. In the first stage, Sylgard 184 PDMS and PDMS-St components were mixed in a ratio of 10:1 and 1:1 respectively, properly stirred, and placed in a desiccator for 20 minutes to extract gases from the pre-polymer gel. Next, samples of NW arrays were covered with pre-polymer Sylgard 184 and PDMS-St and centrifuged in an Eppendorf machine during 40-60 min at 5000 rpm. The thickness of the PDMS films should be lower than the NW average length for the single-walled carbon nanotube (SWCNT) contact application. After the coating, the sample was baked in an oven at 65 – 80 °C for 4 – 8 hours for PDMS polymerization. In addition, PDMS-St in comparison with PDMS 184 has improved tensile strength (2.9 - 4.8 MPa), low adhesion, and better elasticity (110-150%) [6].

Scanning electron microscopy (SEM) was used to control the length of the revealed parts of the nanowires. In the next stage, the membrane was etched in a radio frequency (RF) plasma mixture of O₂ / CF₄ gases to remove PDMS wetting at NW top parts. The ratio of the O₂/CF₂ fluxes was 20/40 ml/s respectively, the period of etching was 20 seconds, and the gas discharge power was 500 W.

Transparent conductive electrodes were applied using SWCNT blankets of 90 nm thickness synthesized by floating catalytic chemical vapor deposition (FC-CVD) [7,8]. SWCNT blankets are an excellent candidate for flexible and stretchable LED electrodes because of their high conductivity, transparency (80-90%), and elastic properties. Moreover, SWCNT contacts allow stacking flexible LEDs of different color channels owing to contact high transparency. In the figure 1b can be seen the contact between NWs top parts and SWCNT blanket. After the upper contact fabrication, the NW/PDMS membrane was peeled from the substrate by a razor blade. After the peeling, NWs on the rear surface of the membrane stick out by about 0.5 μm. Hence, SWCNT contact pads may be applied immediately (figure 1a).

![Figure 1](image)

**Figure 1.** The SEM images of the upper part of the structure without (a) and with (b) SWCNT, SEM image of the SWCNT blanket on the top parts of the NWs (c) and the scheme of the NWs encapsulated into the flexible PDMS polymer (d).
3. Characterization
In order to determine the electrical and optical properties of the light-emitting GaP/GaPAs NW array encapsulated in the PDMS I-V and electroluminescence (EL) measurements were performed.

![I-V curve](image1)

**Figure 2.** Representative I-V curve of functional NW/PDMS membrane LED.

We consider SWCNTs to have a p-type of conductivity [9]. The shape of the I-V curve (figure 2) with a knee bias at 2.25 V indicates the presence of a Schottky barrier, which is most likely associated with the SWCNT/n-doped GaP interface.

The forward curve can be explained by the reverse Schottky barrier between SWCNT and n-GaP. The p-GaP/SWCNT interface may be considered as Ohmic contact. The I-V characteristics were performed using the continuous mode of the source. The nature of this barriers and I-V characteristics were detailedly discussed in [3].

![EL spectrum](image2)

**Figure 3.** EL spectrum of GaP/GaPAs NW/PDMS membrane LED.

Also, the fabricated LED membrane demonstrates the EL mainline in the red spectral range (figure 3), the EL spectrum peak is located between 625 nm and 675 nm. Figure 4 shows photo of an operational membrane LED. All the measurements were achieved at room temperature (25 °C). Although we assume that the temperature of NWs increases during the working regime. The special
cooling system was not utilized. The area pumped by the current of GaP/GaPAs NW/PDMS membrane was about 1 mm² x 0.5 mm² = 0.5 mm² (figure 3).

Figure 4. Actual photo of the operational LED sample.

4. Conclusions
The manufactured flexible PDMS membranes with the encapsulated LED GaP/GaPAs nanowires demonstrated red emission in the range of 625-675 nm. The measured I-V curves have diode characteristics. This novel type of LEDs might have a crucial impact on flexible optoelectronics and future RGB display technology.

Acknowledgements
VN thanks the Russian Foundation for Basic Research (RFBR project № 19-32-60040) for PDMS/NW membrane fabrication. ASM and RMI thank the support from the Russian Science Foundation (grant 20-19-00256) for PDMS-St synthesis. The authors thank the Ministry of Science and Higher Education of the Russian Federation (FSRM-2020-0005).

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