Processing and characterization of GaP nanowires encapsulated into a PDMS large-scale membrane for flexible optoelectronics

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Abstract. This paper presents the methods of fabricating arrays of semiconductor III-V nanowires transferred into a flexible polydimethylsiloxane membrane. Molecular beam epitaxy was used to synthesize GaP nanowires. The synthesized nanowire arrays were encapsulated into a silicone membrane by a heavy load swinging-bucket centrifuge. For optoelectronic applications, the nanowire/polydimethylsiloxane membranes were contacted with single-walled carbon nanotubes, peeled from the substrate, then the second carbon nanotubes contact was formed. For optical experiments, the nanowire/polydimethylsiloxane membranes were bonded to supporting polydimethylsiloxane films by oxygen plasma treatment, and then easily released from the substrate by unsticking. The obtained membranes have a high practical potential in flexible optoelectronics.

1. Introduction

Nowadays, the demand for flexible optoelectronics is growing every year. Flexible optoelectronic devices allow integration with complex form surfaces and biomedical implants. For example, paper-like displays, foldable touch screens, wearable biosensors, antennas, and surgeon implants are extensively studied [1-3]. Today, the most developed flexible technology is based on organic materials [4]. For instance, organic light-emitting diodes (OLEDs) that are commonly used, have a low manufacturing price and a relatively good performance. However, OLEDs are still behind inorganic materials in terms of values of quantum efficiency (EQE) of 2-30% and brightness of $10^2$-$10^4$ cd/m², and a limited lifespan [5,6]. Meanwhile, flexible devices based on inorganic thin films are challenged by a highly complicated transfer to flexible carriers, since it requires laborious operations of etching, structuring, and separation from the growth substrate. The use of nanowires (NWs) array embedded in a flexible polymer is a promising way to solve this problem since it combines the efficiency of inorganic materials and simplicity to manufacture large-scale flexible devices.
2. Fabrication

Self-catalyzed GaP NWs arrays were synthesized by molecular beam epitaxy on 3" Si(111) wafers via a vapor-liquid-solid growth mechanism. GaP and Si have a low lattice mismatch (0.37%) that facilitates epitaxial growth of NWs with a high crystallinity on widely spread Si substrates. However, GaP is an indirect bandgap semiconductor with $E_g=2.27$ eV at 300K [7], and direct bandgap GaPAs or GaPN(As) films grown on silicon are not widely spread due to the high lattice mismatch between such alloys and GaP buffer layer grown on Si. NW geometry, however, allows a combination of very different crystalline materials of high quality because of the relaxation of stress at NW sidewalls.

To obtain n-conductivity, NWs were intentionally doped by introducing a silicon flux during the growth. It was shown, that despite the amphoteric nature of Si dopant in III-V compounds predominantly n-type conductivity is observed in III-phosphide alloy NWs [8]. More detailed information about the synthesis procedure can be found elsewhere [9,10].

In order to embed GaP NWs into flexible silicone, the graft-copolymers of polydimethylsiloxane and polystyrene (PDMS-st) were G-coated in a swinging-bucket centrifuge instead of a standard spinner [11]. The common spin-coating method is not suitable for dense NW array encapsulation due to a high capillary effect preventing pre-polymer gel penetration between NWs. Thus, G-coating is more suitable, it presses the PDMS-st pre-polymer gel between NWs thanks to the centrifugal force direction along the NWs. Moreover, this method preserves NW verticality and allows achieving the record-thin polymer films.

First, the Sylgard 184 PDMS and PDMS-St were mixed in the ratio of 10:1, perfectly stirred, and left in a desiccator for 20 minutes to extract air bubbles. Second, the array of the NWs was covered by the PDMS-st pre-polymer gel and placed into the heavy load centrifuge (Beckman Coulter Avanti J-HC with a Rotor JS-4.2 A) at 4200 rpm for 40 minutes. After PDMS-St deposition, the samples were crosslinked in a muffle oven at 80 °C for 4 h. It should be noted that the thickness of the coated PDMS must be lower than the NWs length for application of single-walled carbon nanotubes (SWCNT) contacts to GaP NW top parts. To control the length of the revealed parts of the nanowires the scanning electron microscopy (SEM) was used (Zeiss SUPRA 25). The achieved length of the NWs top parts can be adjusted during the coating procedure in the centrifuge machine and by the plasma treatment. The membranes were etched in a radio frequency (RF) plasma mixture of O$_2$/CF$_4$ gases. The ratio of the O$_2$/CF$_4$ fluxes was 20/40 ml/s respectively, the period of etching was about 20 seconds, and the gas discharge power was 500 W.

SWCNT films were used as flexible, conductive, and transparent electrodes because of their high conductivity, transparency, and elastic properties [12]. SWCNT films of 90 nm thickness were synthesized by floating catalytic chemical vapor deposition (FC-CVD) on nitrocellulose filter paper [13, 14]. The SWCNT contact pads of appropriate size were cut and directly applied onto the sample. After the upper contact fabrication, the NW/PDMS membrane was peeled from the substrate by a steel razor blade (figure 1). After the peeling, NWs on the rear surface of the membrane stuck out by approximately 0.5 µm. Hence, SWCNT contact pads may be applied immediately. Figure 1(f) presents an optical image of a released GaP NWs/PDMS-St membrane of a 3 square inch area.

Large area PDMS membranes with embedded III-V NWs can be also used for optical applications such as IR-to-Vis converters based on second harmonic generation [15]. To fabricate such a converter, the NW/PDMS membranes and 50-150 µm thick PDMS cap films were treated in O$_2$ plasma to modify the surface of PDMS. Then the cap film was put gently on the PDMS/NW membrane forming strong Si-O-Si bonds due to the O$_2$ plasma surface modification and the whole structure was unstuck from the substrate (figure 2).
3. Characterization

After the fabrication procedure, the I-V measurements of flexible membranes were performed using a Keithley source meter. The results of measurements for several randomly positioned contact pads are presented in figure 3. The representative I-V results are presented in figure 3. The size of the contact pads was about 0.25 mm².
Figure 3. I-V characteristics of the flexible large-scale membrane were measured on the different contact pads (a-d). Colored lines describe the number of measurements.

The form of the current-voltage curve can be explained by the Schottky barrier presence between SWCNT and n-GaP NWs. We consider that SWCNT has a p-type of conductivity [16]. Also, the Schottky shape of the curve indicates that current goes through the NWs and is collected on the SWCNT pads avoiding the shunting effect in the PDMS layer between contiguous NWs. In addition, after 2 months the obtained characteristics were reproduced, and it showed the stability of the electrical properties of the membrane (figure 4) up to 8 V with the current density of 3 A/cm².

Figure 4. Measured I-V characteristics of the contact pads of the PDMS/GaP flexible membrane recently after the fabrication (blue) and after 2 months (red).
As for the NW/PDMS IR-to-Vis converters, optical characterization of the flexible PDMS/GaP membrane was performed to determine specifically spectral dependence of the SHG in GaP NWs having a high value of the quadratic nonlinear susceptibility ($\chi^2 \approx 70\, \text{pm/V}$ at approximately $1\, \mu\text{m}$ wavelength) and the broad range of transparency. Because of almost similar refractive indexes of GaP ($n \approx 3.4$) and Si ($n \approx 3.9$), it results in leakage of optical power in NWs that is transferred into the Si substrate. It might be a limiting factor of this design. However, embedded GaP NWs into the flexible PDMS polymer solves this problem and provides new applications of functional optoelectronics [15]. The results are presented in figure 5.

![Figure 5](https://example.com/figure5.png)

**Figure 5.** The experimental spectral dependence of the GaP SHG (white dots, left axis). Red and blue curves describe the second-order susceptibility and absorption coefficient of the bulk GaP [17] respectively.

4. Conclusions
In conclusion, this work demonstrated a functional large area flexible membrane based on vertically oriented GaP NWs in the silicon matrix that can be used for LEDs or IR-to-Vis light converters. The developed method has a high potential for applications in flexible optoelectronics.

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