Modified silicone rubbers for fabrication and contacting of flexible suspended membranes of n-/p-GaP nanowires with single-walled carbon nanotube transparent contact

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Abstract. This work proposes new chemical and mechanical materials and techniques for III-V semiconductor NW/silicone membrane formation and optoelectronic device fabrication. Molecular beam epitaxy (MBE)-synthesized n-, p- and i-GaP NWs were encapsulated by introduced G-coating method into synthesized polydimethylsiloxane-graft-polystyrene and released from the Si growth substrate. The fabricated membranes were contacted with different materials including single-walled carbon nanotubes or ferrocenyl-containing polymethylhydrosiloxane with and without multi-walled carbon nanotubes doping. The electrical connection of the fabricated membranes was verified by electron beam induced current (EBIC) spectroscopy. The developed methods and materials can be applied for fabrication of high quality flexible inorganic optoelectronic devices.

1. Introduction

The appealing properties of organic light emitting diodes (OLEDs), i. e. relatively easy and inexpensive fabrication, and efficient electroluminescence (EL) allowed the OLED-based industry to conquer a significant market share. For instance, modern smartphones are mostly produced with the OLED displays.

However, organic materials are far behind the inorganic materials in terms of stability and external quantum efficiency (EQE) of EL in optical range, especially in blue and red region, which for inorganic devices becomes close to 100%. Inorganic LEDs based on compounds of arsenides, nitrides, phosphides etc. are envisioned to be the materials for the LEDs with the efficiency close to the theoretical limit. The recent commercial application of OLEDs instead of inorganic materials is explained mainly by difficulties of combination of different radiative materials necessary for an RGB full color screen. Indeed, the mainstream thin film technology is hard to adapt for small high resolution screen, because it requires either advanced post-growth processing, or combination of very different crystalline materials. The flexible devices fabrication based on thin films imposes even greater complications, i. e. ultra thin wafer epitaxy or release of the synthesized material from the wafer [1].

Nanowire (NW) or microwire (MW) design of inorganic devices has several significant advantages, especially for substrate-free device fabrication. Wires have a small footprint, therefore they can be mechanically removed from the initial growth substrate. High surface to volume ratio leads to an effective relaxation of the elastic strain due to the lattice mismatch of III-V heterostructures, therefore low structural defect concentration can be achieved even for a high lattice mismatch. Core-shell wire heterostructures also have effective light extraction and current injection [2], which is very important for optoelectronic applications, e. g. LEDs. The pixel contacts to membranes with different color channels could be provided independently, thus the elastomer/NW devices can be considered as inorganic analogue to OLED devices.

The main reason is essentially the difficulties in fabrication and functionalization of NW devices, which are even more pronounced for membrane devices. Indeed, compared to a thin film device the elastomer/NW LED device is basically an array of billions of independently operating NWs LEDs, which requires complicated contacting to achieve a high yield, i. e. the radiating/dim NW ratio. The yield is typically low because an LED works in the steep region of I-V curve, and therefore a small variation of series resistance and material composition due to the inhomogeneous distribution of NW parameters, i. e. voltage applied to
individual NWs, leads to a significant variation of current [3]. Membrane devices also have a problem of mechanical stability of contacts, and elastomer materials prevent high temperature annealing, required to achieve the ohmic resistance in many semiconductor-metal material systems.

This work is devoted to the new chemical and mechanical materials development for III-V semiconductor NW/PDMS-st membrane fabrication. The introduced G-coating method of NW encapsulation into synthesized polydimethylsiloxane-graft-polystyrene allowed an easy release of NW membrane from the Si growth substrate. Different materials including single-walled carbon nanotubes, ferrocenyl-containing poly(methylhydrosiloxane) with and without multi-walled carbon nanotubes doping were used to contact NWs membranes.

2. Methods

Epitaxial arrays of GaP NWs were synthesized by self-catalyzed vapor-liquid-solid (VLS) mechanism in solid source molecular beam epitaxy (MBE) process using Veeco GEN-III MBE machine. Valved phosphorus cracker was used to produce P2 molecular flux at cracking temperature of 900°C.

Polydimethylsiloxane-graft-polystyrene (PDMS-St) was synthesized in accordance with procedure published in [4]. Freshly distilled styrene, \( \alpha,\omega \)-bis(trivinylsiloxy)polydimethyldisiloxane, azobisisobutyronitrile (AIBN) and ethanol were loaded into a three-necked flask equipped with a reflux condenser, stirrer, and heater. The styrene loading was 40 wt.% of \( \alpha,\omega \)-bis(trivinylsiloxy)polydimethyldisiloxane, and the AIBN loading was 0.8 wt.% of the total reaction mass.

The common method to encapsulate NW arrays into polymer matrix is spin-coating [5], i.e. polymer drop-casting followed by thinning the film in vertical centrifuge similar to the photoresist application routine. The spin-coating method allows to achieve a good encapsulation of long (more than 20 µm) and low density (less than 0.1 NW per sq. µm) NW arrays, however, short and/or dense NW array embedding is challenging due to the high PDMS viscosity. This viscosity can be reduced by diluting PDMS with methylene chloride, toluene, hexane or other solvents, allowing spin-casting of thin (thinner than 3 µm) PDMS films. In this paper we propose a different approach for NW array encapsulation with the use of swinging bucket centrifuge, where the thinning force is perpendicular to the sample surface (Figure 1). The relative centrifugal force in bucket centrifuge can be higher compared to commonly used spin-coaters and reach 5-10 thousand G-force for standard swinging bucket rotors and up to 1 million G-force in ultracentrifugal rotors. For convenience and to underline similarity with gravity force we propose to call this method G-coating by analogy with spin-coating. The advantage of G-coating for the NW embedding is the high pressure applied to PDMS-St, which fills the space among the NWs.

![Figure 1. Spin-coating in spinner (a) and G-coating in swinging bucket centrifuge (b).](image-url)

The PDMS-St/NW fabrication started with PDMS-St (component A) and cross-linker (component B) mixing 1:1 mass ratio, followed by debubbling in the exicator for 30-40 min. Then the prepared PDMS-St mixture was dropped onto the samples and G-coated at approx. 4500 G-force for 60 min. until the sample surface turns matt due to the light scattering by revealed NW top parts. After PDMS-St deposition, the samples were cross-linked in the oven at 80°C for 2 hours or during the night. The prepared PDMS-St/NW structures were etched in 5 cycles 40 s etching / 60 s interruption sequence for cooling, mixture of 15 and 40 ml per min. flux of O2 and CF4, respectively, and 150 mW RF plasma in order to remove PDMS-St wetting of the NW top parts to allow further electrical contacting.
To compare different contacting strategies, we deposited onto the NW top parts (i) Cr/Au/Cr 5/50/20 nm metal layers, (ii) SWCNT film with 40 nm thickness, 80% transparency and 250 Ω·cm sheet resistance [6], (iii) pristine FPS, and (iv) FPS mixed at 100:1 mass proportion with MWCNT with 20 µm and 20 nm average length and width, respectively. Then the PDMS-St/NW membranes were mechanically peeled from the Si wafer with a razor blade and flipped onto an arbitrary holder. The bottom parts of the NWs were protruding from the membranes, and their surface was not covered with the PDMS-St, therefore after the membrane release the samples were ready for the bottom contact deposition. In order to perform a consistent analysis and facilitate comparison of the contacted membranes, the bottom contact material was chosen the same for all (i-iv) samples. The best candidate is SWCNT contact due to its high elastic properties, conformal coverage of the NWs, high conductivity and transparency for both optical and SEM microscopy. The SWCNTs are also the envisioned contact for the optoelectronic devices, allowing to stack the PDMS-St/NW membranes with each other or different material systems in composite structures due to SWCNT contact transparency. The design of the fabricated samples is shown in Figure 2.

After top contact fabrication all (i-iv) samples were processed in a similar way. The samples were peeled with a razor blade, flipped onto an arbitrary holder, i.e. a piece of Si wafer, Al plate or glass, and the SWCNT contact pads of average size approx. 1 mm² were applied. Due to mechanical instability and advanced chemistry the samples were controlled at each step by optical and electron microscopy.

Finally, we fabricated p-GaP:Be PDMS-St/NW membrane sample similar to n-GaP sample (ii), i.e. with SWCNT contact pads on both sides. The I-V characteristics for the p-GaP membrane were measured in order to define the ohmicity of the contact of SWCNT to p-GaP, which was expected to have low barrier or even to be ohmic due to the hole conductivity of the SWCNT [7].

Current-voltage characteristics of fabricated samples (i-iv) were measured (Figure 3). Because all the contacts are expected to have electric barrier to the n-GaP material, the strongly nonlinear behaviour of the I-V curves may be associated with the reversed Schottky barrier characteristic. The sample (i) demonstrated lower knee bias in comparison to other samples, which we associate with high surface state density at the interface of Cr/n-GaP NW. The positive voltage branch of the sample (i) and symmetric curve of the sample (ii) demonstrated knee value at 5 V, which we attribute to reversed current in SWCNT/n-GaP Schottky barrier. The sample (iii) demonstrated instabilities of the current at positive applied bias, which may originate from the mechanical instability or the piezo or thermal striction of the PDMS-St membrane.
material, similar instabilities at I-V curve, accompanied by EL blinking, were also observed for LED membrane devices [3]. The sample (iii) demonstrated a high knee voltage of 7-8 V and relatively low current. Sample (iv) demonstrated an I-V curve shape similar to sample (ii), but less current and higher knee voltage. The FPS and FPS/MWCNT contacts demonstrated a high mechanical stability. The calculated current through individual wires and the derived current density of the measured samples are presented in Table 1.

Figure 3. Current-voltage curves of n-GaP : Si samples (i-iv). The photographs in the insets demonstrates the corresponding PDMS-Si/NW membrane (grayish yellow), and three SWCNT contact pads (gray squares); the size of contact pads is about 0.25 mm². Samples have similar SWCNT contact pads on the NW bases, and different top contacts: (i) Cr/Au/Cr metallic contact, (ii) SWCNT contact pads, (iii) continuous FPS contact, (iv) continuous FPS/MWCNT contact.

To supply the main n-GaP : Si NW sample series of the presented work with additional comparison, we processed p-GaP : Be NW similar to samples (i-ii). The p-GaP NW sample has different morphology, namely 3 µm and 250 nm average NW height and width, respectively. The average height and width are 3 µm and 250 nm, respectively. The NWs feature a Ga metallic droplets on top of them, which remain after the epitaxial growth interruption.

The measured I-V curves are presented in Figure 4. The sample with metallic contact demonstrated higher resistivity in comparison to the SWCNT sample, the knee voltage is similar for both samples and is estimated to be in the range of 0.5-1 V. We attribute the non-linearity of the I-V curve to the Ga droplets, having small Schottky barriers with the p-GaP material and/or the SWCNT contact. The derived current values are presented in Table 1.
Figure 4. The measured I-V curves of p-GaP:Be NWs in PDMS-St/NW membrane with Cr/Au/Cr (left) and SWCNT (right) top contact. The bottom contact of both samples is SWCNT contact pads. The inset photos show the measured samples.

Table 1. Calculated current through individual NWs and corresponding current densities.

| Sample                        | Current at 1 V above | Current density, mA/cm² |
|-------------------------------|----------------------|-------------------------|
| (i) n-GaP Cr/Au/Cr SWCNT     | 2                    | 4                       |
| (ii) n-GaP SWCNT both sides  | 30                   | 60                      |
| (iii) n-GaP FPS SWCNT        | 0.3                  | 0.6                     |
| (iv) n-GaP FPS/MWCNT SWCNT   | 10                   | 20                      |
| p-GaP Cr/Au/Cr SWCNT         | 800                  | 400                     |
| p-GaP SWCNT both sides       | 3200                 | 1600                    |

3. Conclusions
The developed PDMS-St allowed to encapsulate and release cm² size NW membranes. The developed G-coating method was used to produce 10 and 3 µm thick suspended NW/PDMS-St membranes. The fabricated n- and p-GaP NW/PDMS-St membranes were processed with Schottky and near-ohmic contacts, respectively. The developed FPS successfully served as flexible semitransparent contact, MWCNT doping efficiently increased the FPS contact performance. The SWCNT network shown its quality as a transparent electrode with high stability and nearly ohmic contact to p-GaP:Be. The presented work proposes advanced chemistry, membrane, and contact fabrication techniques, which can be adapted for fabrication of NW optoelectronic devices.

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