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### ARTICLE

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### 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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Rubber materials are the key components of flexible optoelectronic devices, especially for the light-emitting diodes based on arrays of inorganic nanowires (NWs). This paper polydimethylsiloxane-*graft*-polystyrene as new flexible substrate of GaP NW array structures. The NWs were encapsulated by the firstly introduced G-coating method to substitute the inefficient mainstream spin-coating. To further exploit the flexibility and the stretchability of the NW/PDMS-St structures, the ferrocenyl-containing polymethylhydrosiloxane (FPS) was synthesized and successfully used as an electrode to the NWs. In order to make an alternative highly efficient transparent electrode, new application of conductive single-walled carbon nanotubes (SWCNTs) was demonstrated. The novel materials and methods demonstrated unsurpassed mechanical stability of the fabricated flexible electronic devices.

#### 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.<sup>1,2</sup> 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,<sup>3</sup> 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.<sup>4</sup> 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.<sup>5</sup>

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.<sup>6–8</sup> 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.9 Core-shell wire heterostructures also have effective light extraction and current injection,<sup>10</sup> which is very important for optoelectronic applications, e. g. LEDs. One of the main attractive features of NW devices is the possibility to combine very different materials, e.g. nitrides and arsenides or phosphides. The NWs can be encapsulated into a polymer matrix (*i.e.* elastomer)<sup>11,12</sup> and then released from the wafer. The elastomer/NW membrane can then be electrically connected with conductive transparent electrodes,<sup>7</sup> and the membranes of different materials may be stacked onto each other to form composite device with multiple line EL. 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.

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Despite the high attractiveness, the early demonstrations of membrane devices based on encapsulated wires did not result in effective device obtaining and usually researchers do not show significant improvement in following papers.<sup>5,6</sup> 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.<sup>13</sup> 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.14

In order to find a solution to the problems of membrane device creation, we developed encapsulation and release technique suitable for few  $\mu m$  thick membranes. The crucial point of our research is the application of advanced silicone chemistry for the specific problems of elastomer/NW membrane fabrication. Typical polydimethylsiloxane (PDMS) rubbers including Dow Corning Sylgard 182 or 184<sup>15</sup> are high elastic (elongation at break L = 160-255%),<sup>16-19</sup> but not very strong (tensile strength  $\sigma = 0.02-0.25$  MPa)<sup>16-19</sup> and tacky to substrates that makes them unsuitable to produce very thin and nonadhesive membranes. The use of copolymers with different vinyl monomers can rectify the problems related to silicone durability and adhesion. Based on our previous data and experience,<sup>16-20</sup> cross-linked graft-copolymers of PDMS and polystyrene (PDMS-St) have improved tensile strength  $(\sigma = 2.9-4.8 \text{ MPa})$ ,<sup>20</sup> good elasticity (L = 100-150%)<sup>20</sup> and low adhesion that allow an easy release from the initial growth substrate.

Apart from suitable polymer matrix material, an adequate encapsulation method is on demand for a high-quality **NW** membrane fabrication. The most common method to cover **NWs** with elastomers is spin-coating,<sup>7,21</sup> and for the dense arrays of **NWs** viscous polymers can hardly penetrate the space between the wires due to a high capillarity effect. In this paper we introduced the new *G-coating* method of **NW** encapsulation. In this method a high pressure of 4-5 thousand G-force pushes the polymer to fill the space between **NWs**, allowing effective encapsulation of > 10 NW/µm<sup>2</sup> dense **NW** arrays.

For further development of elastomer/NW device fabrication, advanced transparent flexible conductive electrodes are required. Different strategies were introduced in literature, including thin and flexible ITO,<sup>22</sup> semitransparent metals, silver nanowires and graphene,<sup>23</sup> carbon nanotubes (CNT)<sup>24</sup> etc. In this paper, we focus on single wall CNT (SWCNT) and ferrocenyl-containing polymethylhydrosiloxane (FPS) as contacting layer. This contact can be further improved with

diluted multi wall CNTs (MWCNTs), having high in-plane development of curable conductivity. The silicone (co)polymers with electroactive fragments in their structure is highly perspective for electrostatic discharge (ESD) protective materials for electrostatic-sensitive devices and power lines,<sup>25,26</sup> active layers for modern sensing electronic devices<sup>27–</sup> <sup>29</sup> and biomedical implants.<sup>30,31</sup> Thus, the integration of metals into a polysiloxane chain can directly influence its electronic and optical properties.<sup>25,32,33</sup> For instance, self-curable polysiloxanes with redox-active ferrocenyl moieties were synthesized.<sup>25</sup> They are attractive materials primarily due to the possibility of self-cross-linking, the application as a liquid contact (which is mechanically reliable and easy for use), high compatibility with PDMS substrate, as well as the ability to combine ferrocenyl-containing silicone rubbers with other materials, such as multi-walled carbon nanotubes, in order to achieve high lateral conductivity.

The main goal of this work was a synthesis of the advanced silicon rubber specially for the membrane device fabrication. In order to complete this task, a demonstration of electrical current transport through the NWs encapsulated in the polymer matrix was required. However, the electrical current can go through shuntings or other defects of the polymer/NW membrane system (e. g. NW surface or interface states in polymer/NW border). Therefore, for a direct demonstration, that the fabricated membranes feature desirable electrical performance, i.e. the current spreads through the front contact layers, then goes inside the NWs and finally is collected by the rear contact, we made a high Schottky barriers for both/one side of the membranes. In this case we have a distinguishable signature in the I-V curves, and EBIC mapping is possible. Alternatively, a low Schottky or an absence of it (which is, actually, desirable in the final optoelectronic devices) is very difficult to distinguish from the shunting and the samples are not suitable for the EBIC microscopy, therefore we discuss the fabricated samples with ohmic contacts after demonstrating reliable Schottky contacting.

#### **Results and discussion**

For the demonstration of **NW/PDMS-St** membrane fabrication with effective electrical contacts we have chosen n-GaP : Si **NW**s due to the expected high Schottky barrier with **SWCNT**s. SEM images of the **NW**s are presented in Fig. 1a, they demonstrated 10  $\mu$ m and 130 nm average height and width, respectively.

The **NW** array have significantly inhomogeneous **NW** height distribution typical for self- induced Ga-catalyzed growth. Therefore, after G-coating encapsulation into **PDMS-St** the lower **NW**s were buried and only the highest **NW**s were revealed after CF<sub>4</sub>/O<sub>2</sub> RF plasma etching, required to remove **PDMS-St** wetting layer from the **NW** tips in order to fabricate the ohmic contacts (Fig. 1b, 1c and 1d). The average density of the contacted **NW** array is estimated to be 0.005 NW/µm<sup>2</sup>, so after contact fabrication the calculated current density was derived using this value.

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After the membrane release, the Si substrates were studied with SEM to control **NW**s transfer to the **PDMS-St**. The SEM images showed no vertical **NW**s (Fig. 1e), the chaotically laying **NW**s can be attributed to the parasitic non-vertical **NW** growth.

Further in-depth n- and p-GaP **NW**s structural characterization will be published elsewhere. To compare different contacting strategies, we deposited onto the **NW** top parts (i) Cr/Au/Cr metal layers, (ii) **SWCNT** film, (iii) pristine **FPS**, and (iv) **FPS** mixed with **MWCNT** (Cr/Au/Cr metals were chosen to form Schottky with n-GaP **NW**s). Current-voltage characteristics of the fabricated samples (i-iv) were measured (Fig. 2). 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.<sup>34</sup> 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.<sup>13</sup> 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.

To demonstrate ohmic contacting with **SWCNTs**, we processed p-GaP : Be **NW**s similar to n-GaP samples (i-ii). The p-GaP **NW** sample has different morphology (Fig. 3), namely 3  $\mu$ m and 250 nm average **NW** height and width, respectively. The average height and width are 3  $\mu$ m and 250 nm, respectively. The **NW**s feature a Ga metallic droplets on top of them, which remain after the epitaxial growth interruption.



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**Fig. 1** SEM images:  $\mathbf{a} - SEM$  image of the cut edge of the as-grown n-GaP : Si NWs on Si wafer;  $\mathbf{b} - 45^{\circ}$  angle SEM image of n-GaP : Si NW array encapsulated into PDMS-St membrane;  $\mathbf{c} - SEM$  image of Cr/Au/Cr contact on the top side of the n-GaP PDMS-St/NW membrane (sample (i));  $\mathbf{d} - SEM$  image of SWCNT contact pad with silver lacquer droplet (left) on the top side of n-GaP : Si NW/PDMS-St membrane (sample (ii)), bright contrast dots in the right area correspond to contacted with SWCNTs NWs;  $\mathbf{e} - 45^{\circ}$  tilted SEM image of the Si substrate of n-GaP : Si NW sample after the membrane release;  $\mathbf{f} - SEM$  image of the control non-doped GaP NW sample with similar to n-GaP NW sample morphology.



Fig. 2 Current-voltage curves of n-GaP : Si samples (i-iv). The photographs in the insets demonstrates the corresponding PDMS-St/NW membrane (grayish yellow), and three SWCNT contact pads (gray squares); the size of contact pads is about 0.25 mm<sup>2</sup>. 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.



Fig. 3 SEM image of the cut edge of the as-grown p-GaP : Be NWs on Si wafer.



Fig. 4 45° angle SEM image of p-GaP : Be NW array encapsulated into  $\ensuremath{\text{PDMS-St}}$  membrane.



Fig. 5 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.



Fig. 6 The measured I-V curve of the control non-doped GaP NW sample. The photograph in the inset demonstrates the PDMS-St/NW membrane (grayish yellow), and three SWCNT contact pads (gray squares); the size of contact pads is about 0.25 mm<sup>2</sup>.

The **NW** array has higher homogeneity of **NW** height distribution because the Ga droplets were not completely spent. After **PDMS-St** encapsulation the revealed **NW** array is presented in Fig. 4. The estimated **NW** density is 0.0125 NW/ $\mu$ m<sup>2</sup>.

The measured I-V curves are presented in Fig. 5. 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 calculated current through individual wires and the

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derived current density of the measured samples are presented in Table 1.

In order to prove that the measured current originates from **NW** electrical connection and not from shunting through possible cracks in the PDMS-St membrane, a control nondoped GaP NW sample with both side SWCNT contact was processed. The morphology of the control sample is very similar to n-GaP NWs, Fig. 1a and 1f, respectively, so an accurate comparison is possible. The sample was processed similar to the best performance sample (ii), the measured I-V curve is presented in Fig. 6. The signal is below the noise level, the 150 pA current at the turning on is a typical Keithley 2400 error due to the electrostatic discharge. We conclude that the control NWs are not conductive, and the n-GaP NW/PDMS-St membranes analyzed above demonstrated current through the NWs and not through possible shunting. It should be mentioned that for all samples we achieved a stable and robust I-V curve without any abrupt peaks and droops which could be associated with the polarization of the polymer, NW piezo strictions, local Joule heating, etc. This confirms that polymer membranes and NW's contacts to conductive layers are mechanically stable what is very important for flexible devices.

 $\ensuremath{\text{Table 1}}$  Calculated current through individual  $\ensuremath{\text{NW}}\xspaces$  and corresponding current densities.

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

In order to prove electrical connection between the **NW** array embedded into **PDMS-St** membrane and the different contacting layers, EBIC measurements were performed, so the Schottky barrier build-in field was tested.<sup>35</sup> The EBIC measurements for **PDMS-St/NW** membranes is very challenging mainly due to mechanical instability, charging and low magnitude of the signal. However, for the reported work low resolution EBIC is sufficient to prove the electrical connection of the **NW** array and the existence of contact barriers, provided the noise level allows to distinguish EBIC signal and attribute it to **NW** location sites. The Fig. 7 and 8 demonstrates SEM images and EBIC maps of the samples (i-ii). The signal resolution allowed to attribute the EBIC signal contrast to the **NW** cites in SEM image. The signal amplitude is low due to the operation in the reversed diode characteristic

curve, however, it allows to detect the presence of a Schottky barrier, *i.e.* the electrical connection to the **NW**s.

#### Experimental

#### **GaP NWs synthesis**

Epitaxial arrays of GaP **NW**s were synthesized by self-catalyzed vapor-liquid-solid (VLS) mechanism in solid source molecular beam epitaxy (MBE) process using Veeco GEN-III MBE machine.

#### PDMS-St synthesis and cross-linking

PDMS-St was synthesized in accordance with procedure



Fig. 7 SEM image (left) and EBIC map (right) of the sample (i) with metallic contact, bright contrast of EBIC map is attributed to electrically connected wires. 10 kV e-beam acceleration voltage.



Fig. 8 SEM image (left) and EBIC map (right) of the sample (ii) with both side SWCNT contact, dark contrast of EBIC map in red circles is attributed to electrically connected wires. 5 kV e-beam acceleration voltage.

published in <sup>20</sup> (Scheme 1). Cross-linking system of **PDMS-St** consists in two components. Component A includes the Karstedt's catalyst solution in vinyl-terminated **PDMS**, which was mixed with **PDMS-St** and stirred to obtain the required catalyst concentration. Component B is the cross-linker composition which contains polymethylhydrosiloxane (**PMHS**). Equal parts of the component A and B were stirred, and then the mixture was placed into a desiccator at room temperature to remove the air bubbles.

#### NW encapsulation

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The common method to encapsulate NW arrays into polymer matrix is spin-coating,<sup>7,21</sup> *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,<sup>21</sup> toluene,<sup>36</sup> hexane<sup>37</sup> or other solvents, allowing spin-casting of thin (thinner than  $3 \mu m$ ) PDMS films.<sup>38</sup> We introduced an alternative method for NW array encapsulation with the use of swinging bucket centrifuge, where the thinning force is perpendicular to the sample surface (Fig. 2). The relative centrifugal force in bucket centrifuge can be higher compared to commonly used spin-coaters and reach 5-10 thousand Gforce for standard swinging bucket rotors and up to 1 million G-force in ultracentrifugal rotors.<sup>39</sup> For convenience and to underline similarity with gravity force we propose to call this method G-coating by analogy with spin-coating (Fig. 9). The advantage of G-coating for the NW embedding is the high pressure applied to PDMS-St, which fills the space among the NWs.

#### PDMS-St/NW fabrication

The **PDMS-St/NW** fabrication started with **PDMS-St** component A and component B mixing, followed by debubbling in the exicator. Then the prepared **PDMS-St** mixture was dropped onto the samples and G-coated, 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. The prepared **PDMS-St/NW** structures were etched by  $O_2/CF_4$  RF plasma in order to

remove **PDMS-St** wetting of the **NW** top parts to allow further electrical contacting.

After top contact fabrication the **PDMS-St/NW** membranes were mechanically peeled from the Si wafer with a razor blade and flipped onto an arbitrary holder for the bottom contact fabrication. 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 was **SWCNT** contact due to its high elastic properties, conformal coverage of the **NW**s, high conductivity and transparency for both optical and SEM microscopy. The **SWCNT**s 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 Fig. 10.

#### SWCNT synthesis

The detailed procedure for SWCNT synthesis is described elsewhere.<sup>40–42</sup> Briefly, SWCNTs were synthesized by aerosol CVD method in a tubular quartz reactor with floating catalytic bed. The synthesized SWCNTs float down in a vertical reactor chamber. The formed SWCNTs reach the bottom of the chamber, where a filter paper is located. When the desirable quantity of the SWCNTs are on the paper, the process is interrupted, and the SWCNTs are pressed on the paper to form a layer. The SWCNT films on the nitrocellulose filter afterwards can be cut to an appropriate geometry and transferred on the sample without additional manipulations by dry application.<sup>43</sup> In order to reduce the risk of accidental shunting, the contact pads were fabricated. The samples (i-iv) had similar SWCNT contact on the rear surface. The sample (ii) featured similarly fabricated SWCNT on both face and rear surfaces.



Scheme 1 PDMS-St and cross-linking.



on Si substrate; (b) encapsulation of NW array into PDMS-St. membrane; (c) NW/PDMS-St. membrane release; (d) SWCNT bottom contact fabrication to NW bases; (e) top contact fabrication (i) Cr/Au/Cr metal, (ii) SWCNT pads, (iii) FPS continuous contact, (iv) FPS doped with MWCNT continuous contact.



#### FPS synthesis and cross-linking

The **FPS** was synthesized by the reaction of catalytic hydrosilylation between **PMHS** and vinylferrocene according to procedure published in <sup>25</sup> (Scheme 2). The obtained **FPS** was dissolved in 2 mL dichloromethane (**DCM**) and applied by drop-casting onto the face surface of the **PDMS-St/NW** membrane before the release from the Si wafer. The **FPS** gel requires evaporation of **DCM** to achieve proper self-cross-linking by the reaction between Si–H groups (Scheme 2).<sup>25,44</sup> After **DCM** evaporation inside a ventilated chemical hood, the samples (iii) were put into an oven for a homogeneous cross-linking of the whole volume of the **FPS**. The fabricated cross-linked **FPS** contact also serves as a good mechanical support, facilitating the **PDMS-St/NW** membrane release from the Si wafer.

#### **Dispersion of MWCNT in FPS**

To increase the inherent **FPS** conductivity we prepared samples (iv) similar to (iii), but with the **MWCNT**s diluted in **FPS**. While in the air the **SWCNT**s exhibit higher conductivity and transparency, the **PDMS/MWCNT** solution demonstrates higher respective properties compared to **PDMS/SWCNT**<sup>45</sup> due to less perturbation of the electron transport in solid solution,

while **SWCNT**s partly loses properties of graphene-like 2D material because of charge carrier scattering.<sup>46</sup>

#### **EBIC** measurements

In order to prove electrical connection between the **NW** array embedded into **PDMS-St** membrane and the different contacting layers, EBIC measurements were performed. It was expected that all contacts to (i-iv) samples should demonstrate electric barrier to the n-GaP material, therefore EBIC mapping allows visualisation of the intrinsic electric fields, provided that the **NW**s are electrically connected. EBIC experiment was performed in Supra 40VP Zeiss SEM setup equipped with Gatan EBIC hard and software coupled with Stanford SR570 sourcemeter, and Kleindiek NC30 micromanipulators.

Detailed procedures for the NW growth, PDMS-St synthesis and cross-linking, PDMS-St/NW fabrication, SWCNT synthesis, FPS synthesis and cross-linking, dispersion of MWCNT in FPS and fabrication of (i-iv) and p-GaP samples are described in detail in the ESI.

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#### Conclusions

The developed **PDMS-St** allowed to encapsulate and release cm<sup>2</sup> size **NW** membranes. The introduced 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 electrical connection of the **NW** array in the **PDMS-St** membrane was proven by control samples processing and EBIC microscopy.

The presented work proposes advanced chemistry, membrane, and contact fabrication techniques, which can be adapted for fabrication of **NW** optoelectronic devices.

#### **Conflicts of interest**

There are no conflicts to declare.

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# Journal of Materials Chemistry C Electronic Supplementary Information

## 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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### 1. NW growth

Valved phosphorus cracker was used to produce P2 molecular flux at cracking temperature of 900 °C. Substrate temperature was controlled with a thermocouple, calibrated using temperatures of Si(111)  $7x7 \leftrightarrow 1x1$  phase transitions as a references.<sup>1</sup> To monitor the group-III and -V element fluxes, beam equivalent pressure (BEP) was measured with the conventional Bayard–Alpert vacuum gauge. Stoichiometric P/Ga flux ratio of 6 was evaluated during the growth of planar GaP epilayers on Si(001), as the lower BEP ratios led to the accumulation of Ga droplets on sample surface.<sup>2</sup> Prior to the growth, the wafer was treated by the modified Shiraki cleaning procedure ended by the wet-chemical oxidation in a boiling azeotrope 68% HNO<sub>3</sub> water solution for 5 min at constant boiling point of 120 °C,<sup>3,4</sup> resulting in the formation of a thin surface oxide layer acting as a growth mask for **NW** nucleation.<sup>5,6</sup> After thermal degassing under UHV-conditions in MBE load lock and buffer chambers, oxidized Si(111) substrates were annealed under 790 °C for 30 min in order to create defects in the oxide layer promoting formation of catalytic Ga droplets needed for the self-catalytic VLS NW growth.<sup>7</sup> NW growth was started by simultaneous opening of Ga and P shutters. To obtain n- and p-type conductivity, **NW**s were intentionally doped by introducing the silicon or beryllium flux during the growth, respectively. It was shown, that despite the amphoteric nature of Si dopant in III-V compounds commonly n-type conductivity is observed in III-phosphide alloy NWs.<sup>8,9</sup> Si-doped NWs were grown at a substrate temperature (T<sub>growth</sub>) of 640 °C and V/III ratio of 24. According to our observations introduction of Si-flux do not interrupt VLS growth only slightly affecting **NW** aspect ratio, while the solution of Be in Ga catalytic droplet affects its morphology and leads to the sidewalls wetting.<sup>10</sup> Thus, to keep stable VLS growth of Be-doped **NW**, the growth temperature was increased by 10 °C, while V/III-flux ratio was decreased to 8. Growth was ended by closing Ga shutter and cooling the sample at 30 °C /min under the group-V flux until 400 °C.<sup>11</sup>

### 2. PDMS-St synthesis and cross-linking

**2.1.** Synthesis of PDMS-St. Freshly distilled styrene,  $\alpha, \omega$ -bis(trivinylsiloxy)polydimethyldisiloxane (synthesized according to procedure published in ref<sup>12</sup>), 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 resulting mixture was stirred for 4–5 h at 60–65 °C under argon atmosphere. The initiator AIBN was then decomposed at 80 °C for 2 h, and the solvent together with unreacted styrene were distilled off under reduced pressure (3–5 mm Hg) at 100–110 °C. Synthesized PDMS-St was fully

characterized by nuclear magnetic resonance (NMR) spectroscopy.<sup>12</sup> Yield of **PDMS-St**: 90%; white viscous liquid; viscosity 78 P.

**2.2. Cross-linking of PDMS-St.** Component A includes the calculated amount of the Karstedt's catalyst solution in vinyl-terminated **PDMS** (0.1 M), which was mixed with **PDMS-St** and stirred to obtain the required concentration  $(2.0 \cdot 10^{-4} \text{ M})$ . Component B (cross-linker): **PMHS** (viscosity 0.12–0.45 P) and **PDMS-St** (1:3 mass ratio) were mixed and carefully stirred. The required amounts were calculated for the specific ratio of Si–H and vinyl groups (3:1) in the reaction mixture. 0.5 mL of the component B was added to 0.5 mL of the component A and stirred for 1 min. The mixture was then placed into a desiccator at room temperature until a dry cured product was obtained. The total catalyst concentration in the final silicon rubber samples was  $1.0 \cdot 10^{-4}$  M.

### 3. PDMS-St/NW fabrication

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 O<sub>2</sub> and CF<sub>4</sub>, 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 Om·cm sheet resistance,<sup>13</sup> (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.<sup>14</sup> 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 **NW**s 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 **NW**s, high conductivity and transparency for both optical and SEM microscopy. The **SWCNT**s 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.

For the sample (i), the metallic contact Cr/Au/Cr was chosen considering high adhesion of chromium to the **NW** and **PDMS-St** material. Au is an excellent material in terms of conductivity and plasticity, but Au adhesion to the **PDMS-St** is very low. In order to improve adhesion, Cr cladding layer were introduced. The Cr/Au/Cr contact have a desirable Schottky barrier to the n-GaP <sup>15</sup> material, what allows to distinguish it from shunting and detect proper contacting in electron beam induced current (EBIC) measurements. The metal was deposited with electron-beam physical vapor deposition (for Cr) and thermal evaporation (for Au) using Boc Edwards Auto 500 setup operating at 5x10<sup>-6</sup> mbar.

### 4. SWCNT synthesis

**SWCNT**s were synthesized by aerosol CVD method in a tubular quartz reactor with floating catalytic bed (T = 880 °C; CO as a carbon source, carbon dioxide as a growth promoter, and ferrocene as Fe catalyst precursor). The **SWCNT**s were collected from the outlet of the reactor on nitrocellulose filter (HAWP, Merck Millipore) for a certain time in order to obtain the desired thickness of thin network. The 40 nm thickness of the **SWCNT** film was chosen as a material with high conductivity, transparency, and conformal coverage of the **NW** protruding parts. The **SWCNT** films on the nitrocellulose filter afterwards can be cut to an appropriate geometry and transferred on the sample without additional manipulations by dry application.<sup>16</sup> In order to reduce the risk of accidental shunting, the contact pads were fabricated (1 mm<sup>2</sup> or less in size). The sample (ii) featured similarly fabricated **SWCNT** on both face and rear surfaces.

### 5. FPS synthesis and cross-linking

The **FPS** was synthesized by the reaction of catalytic hydrosilylation between **PMHS** and vinylferrocene according to procedure published in ref.<sup>17</sup> The molar ratio of the Si–H groups and vinylferrocene was selected so that 50% of the hydride Si–H groups remained unreacted. Vinylferrocene (1.5 g, 7.08 mmol) was added to a benzene solution (10 mL) containing 20 µL of a 0.1 M solution of Karstedt's catalyst in xylene in a tube purged with argon. The mixture was stirred at room temperature for 1 h. Then, a solution of **PMHS** (849 mg, 14.15 mmol of –OSiHCH<sub>3</sub>– moieties) in dry benzene (10 mL) was added dropwisely for 1 h. The contents of the tube were sealed and stirred at 40 °C for 24 h. The solvent was removed by rotary evaporation. Yield of **FPS**: 2.35 g (100%); brown viscous liquid. The obtained **FPS** was fully characterized with NMR spectroscopy,<sup>17</sup> dissolved in **DCM** (2 mL) and applied by drop-casting onto the face surface of the **PDMS-St/NW** membrane before the release from the Si wafer. The **FPS** gel requires evaporation of

**DCM** to achieve proper self-cross-linking by the reaction between Si–H groups.<sup>17,18</sup> After 24 h **DCM** evaporation inside a ventilated chemical hood, the samples (iii) were put into an oven at 80 °C for 30 min, resulting in a homogeneous cross-linking of the whole volume of the **FPS**. The fabricated cross-linked **FPS** contact also serves as a good mechanical support, facilitating the **PDMS-St/NW** membrane release from the Si wafer.

### 6. Dispersion of MWCNT in FPS

To increase the inherent **FPS** conductivity we prepared samples (iv) similar to (iii), but with the **MWCNT**s diluted in **FPS**. While in the air the **SWCNT**s exhibit higher conductivity and transparency, the **PDMS/MWCNT** solution demonstrates higher respective properties compared to **PDMS/SWCNT**<sup>19</sup> due to less perturbation of the electron transport in solid solution, while **SWCNT**s partly loses properties of graphene-like 2D material because of charge carrier scattering.<sup>20</sup> For homogeneous dispersion of **MWCNT** in **FPS** the tubes were first dispersed in **DCM** with 2 mm diameter ultrasound probe at 84 W power for 60 min, and then the **MWCNT/DCM** solution was added to **FPS** and ultrasounded at 24 W for 20min. Then the **FPS** with **MWCNT**s was applied to the **PDMS-St/NW** surface and left in the ventilated hood for 24 h for **DCM** evaporation and then baked for 30 min at 80 °C similar to the sample (iii).

### 7. Fabrication of (i-iv) and p-GaP samples

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 mm<sup>2</sup> were applied. Due to mechanical instability and advanced chemistry the samples were controlled at each step by optical and electron microscopy.

To allow stable I-V measurements the samples were put with the **NW** top parts onto a Si wafer with a Au0.85Ge0.15 200 nm conductive layer serving as the bottom electrode. Then small droplets of silver lacquer CDS Electronique L-200 was put on the **SWCNT** contact pads to allow probe tip connection. The high-quality silver lacquer was chosen instead of standard paste or paint because of fast drying, i.e. 10 min., low viscosity facilitating small droplet application, low charging and outgassing inside SEM setup, high adhesion to **SWCNT**s, and traceless removal in acetone.

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**.<sup>21</sup>

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