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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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Table of contents

1. NW growth

Valved phosphorus cracker was used to produce P_2 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.[1] 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.[2] 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_3 water solution for 5 min at constant boiling point of 120 °C,[3,4] resulting in the formation of a thin surface oxide layer acting as a growth mask for **NW** nucleation.[5,6] 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.[7] **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 **NW**s.[8,9] Si-doped **NW**s were grown at a substrate temperature (T_{growth}) 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.[10] 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.[11]

2. PDMS-St synthesis and cross-linking

2.1. Synthesis of PDMS-St. Freshly distilled styrene, α,ω-bis(trivinylsiloxy)polydimethyldisiloxane (synthesized according to procedure published in ref [12]), 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 α,ω-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.[12] 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 ($2.0 \cdot 10^{-4}$ 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_2 and CF_4, 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,[13] (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.[14] 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 [15] 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 $5\text{x}10^{-6}$ mbar.

4. SWCNT synthesis

SWCNTs 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.[16] In order to reduce the risk of accidental shunting, the contact pads were fabricated (1 mm^2 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.[17] 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 $–OSiHCH_3–$ 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,[17] 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.[17,18] 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**[19] 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.[20] 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^2 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**.[21]

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