Electronic Supporting Information

(ESI)

Metal Nanoparticles Reveal the Organization of Single-Walled Carbon Nanotubes in Bundles

Raul D. Rodriguez,[a,b,*] Thomas Blaudeck,[c,*] Jana Kalbacova,[a,b] Evgeniya Sheremet,[d] Steffen Schulze,[d] David Adner,[e] Sascha Hermann,[b,c] Michael Hietschold,[d] Heinrich Lang,[b,e] Stefan E. Schulz,[b,c,f] Dietrich R. T. Zahn[a,b]

a. Semiconductor Physics, Technische Universität Chemnitz, 09107 Chemnitz, Germany.

b. Center for Advancing Electronics Dresden (cfaed), Technische Universität Chemnitz, 09107, Chemnitz, Germany.

c. Center for Microtechnologies, Technische Universität Chemnitz, 09107 Chemnitz, Germany.

d. Solid Surfaces Analysis, Technische Universität Chemnitz, 09107 Chemnitz, Germany

e. Inorganic Chemistry, Technische Universität Chemnitz, 09107 Chemnitz, Germany.

f. Fraunhofer Institute for Electronic Nano Systems (Fraunhofer ENAS), 09126 Chemnitz, Germany.

*** Corresponding author:**

Dr. Raul D. Rodriguez

e-mail: raul.rodriguez @physik.tu-chemnitz.de

tel. +49(0)371.531.39653

Preface

In the Experimental Section of this paper, we refer to previous papers, in which some of the authors comprehensively studied

(i) the dispersion preparation for the aligned deposition of SWCNTs for CNT-FETs (H. B. Yu, S. Hermann *et al.*, *Chemical Physics*, 2012, **408**, 11-16), and
(ii) the synthesis of Au nanoparticles and their stabilization in an organic medium without additional molecular ligands (A. Tuchscherer *et al. Dalton Transactions*, 2012, **41**, 2738-2746), and
(iii) the wafer-level decoration of CNT-FETs with Au nanoparticles (T. Blaudeck, D. Adner *et al.*, *Microelectronic Engineering* 2015, **137**, 135-140)

The experiments on the topic of *this* paper were carried out in parallel to these communications, hence the protocols given in the Experimental Sections as well as the ESIs of the cited papers remain valid. Still, upon suggestion of the Editor and for the courtesy of the readers, in *this* ESI, we present a compilation of the relevant experimental protocols.

A. Experimental Details

A.1 Deposition of SWCNTs

The deposition and alignment of the SWCNTs between electrodes and on plain substrates was performed from aqueous dispersions of SWCNTs (Nanointegris Inc., >98 % semiconducting, length *ca.* 2 µm). The preparation included homogenization and debundeling in sodium dodecyl sulfate (SDS, Sigma Aldrich, ACS/BioXtra grade or comparable) dissolved in deionized water (18 MOhm·cm). A typical dispersion protocol was the following: for homogenization, the bucky paper was undergone tip-ultrasonication (Sonotrode KE76, Bandelin) for ca. 10 min at 60 W (duty cycle: 5 seconds pulse, 5 seconds pause) for ragging the bucky paper into microscopic pieces. Same ultrasonication was employed for ca. 60 min at 40 W (duty cycle: 5 seconds pulse, 55 seconds pulse) to further pluck the SWCNT rags and induce SWCNT debundeling. Finally, centrifugation (2 h at 55000 g) was used to select the SWCNT raw material with the highest degree of debundeling for the transistor fabrication using electrokinetic methods. Optimization of the dispersion process (homogenization, dispersion, and centrifugation) is an ongoing research issue.

A.2 Synthesis of gold nanoparticles and analysis results

For nanoparticle synthesis, triphenylphosphinegold(I)-2-[2-(methoxyethoxy)ethoxy]acetate was prepared according to literature (Ref. [21]). For the nanoparticle preparation, 31.8 mg (0.05 mmol) of the complex were dissolved in 10 mL of triethylene glycol dimethyl ether (triglyme). To the resulting 5 mM solution, a single crystal of silver(I) nitrate was added (approximately 0.01 mg). The reaction mixture was heated to 175 °C with a preheated oil bath and kept at this temperature for 10 min. After cooling, the resulting wine-red solution directly was used for all follow-up procedures. TEM images were recorded with a Fecnai FC20 at an accelerating voltage of 200 kV and are shown in Figure S1.

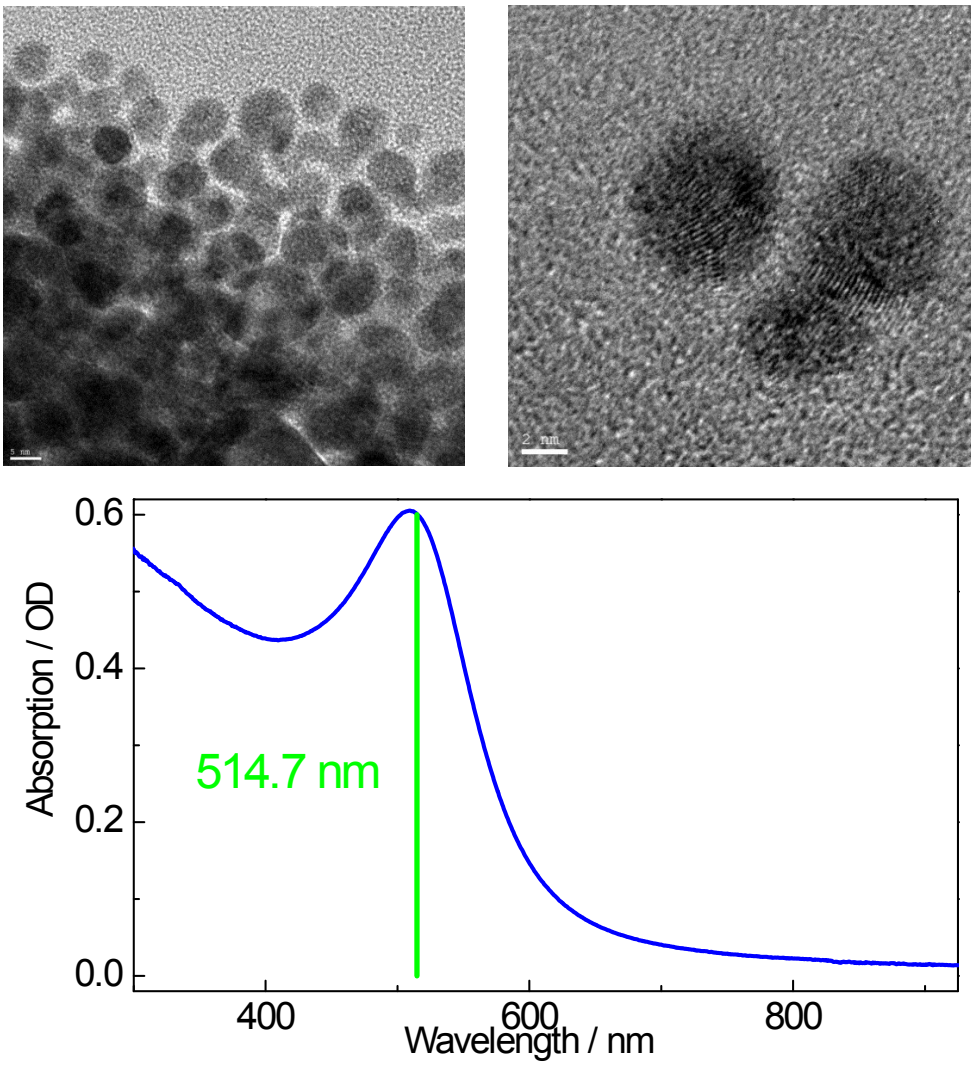

Figure S1: TEM images of gold nanoparticles (left: scale bar 5 nm, right: scale bar 2 nm) (Source: T. Blaudeck, D. Adner et al., *Microelectronic Engineering* 2015, **137**, 135-140). Absorption spectrum of the Au nanoparticles in solution.

The optical absorption spectrum of the samples in dispersion is shown in the Figure S1. The laser excitation is depicted by the vertical line at 514.7 nm.

A.3 Functionalization of wafer-level CNT-FETs with preformed Au nanoparticles

A soft stamp for the on-wafer functionalization was made from polymethyldisiloxane (PDMS) and contained 200 µm wide microfluidic channels connected to a microsyringe pump (nemeSYS) with a flow precision of a few µL per min. On one plane side of the stamp, they were kept open to contact with the wafer surface. For the experiments, the side with the channel opening was aligned onto the silicon wafer in a way maintaining efficient wetting of the CNT-FETs which were designed to align as multiple fingers each along the channel. To maintain the reaction conditions, the wafer with the aligned microfluidic stamp on top was mounted on a heating system with a precision thermostat (Friedr. Freek GmbH) to cycle the wafer temperature up and down in a controlled manner to adjust temperature plateaus between room temperature

and ca. 180 °C with ramps of ca. 10 K min^{-1}. For the functionalization with Au nanoparticles, both a dynamic and a static flow profile (cf. Table S1) were applied, each on Au nanoparticle dispersions at 'ambient' (T = 23 °C, c = 0.5 mmol/L) and 'elevated' (T = 40 °C, c = 5 mmol/L) conditions. In this work, we studied CNT-FETs in two different decoration protocols, as well as a reference sample with CNT-FETs without any functionalization (cf. Table S1).

Table S1: Microfluidic protocols relevant to this paper for the functionalization of CNT-FET transistor channels with Au nanoparticles on wafer (compiled from T. Blaudeck, D. Adner *et al.*, *Microelectronic Engineering* 2015, **137**, 135-140).

Sample ID	**Stage 0** CNT deposition	**Stage I** primary functionalization (referring to Ref. [19])	**Stage II** secondary functionalization Au nanoparticles (referring to Ref. [19])	DI rinsing
F2-K4	YES	**NO**	**NO**	**YES**
F5-K1	YES	**NO**	**YES** 2 h @ 5 µL/min c = 0.5 mM T = 23 °C	**NO**
F4-K4	YES	**NO**	**YES** 2 h @ 0 µL/min c = 5 mM T = 40 °C	**YES**

B. Further local analysis

B.1 Morphological (AFM, SEM) analysis of Au-decorated CNT-FET

Figure S3 shows a zoomed AFM topography image of a CNT-FET before and after decoration with Au nanoparticles. Figure S4 shows a series of CNT-FETs observed in electron microscopy using two different magnifications (100.000-fold, left and 150.000-fold, right). The CNT-FET shown in Figure S3 and Figure S4 is the same as shown in Figure 4d in this paper

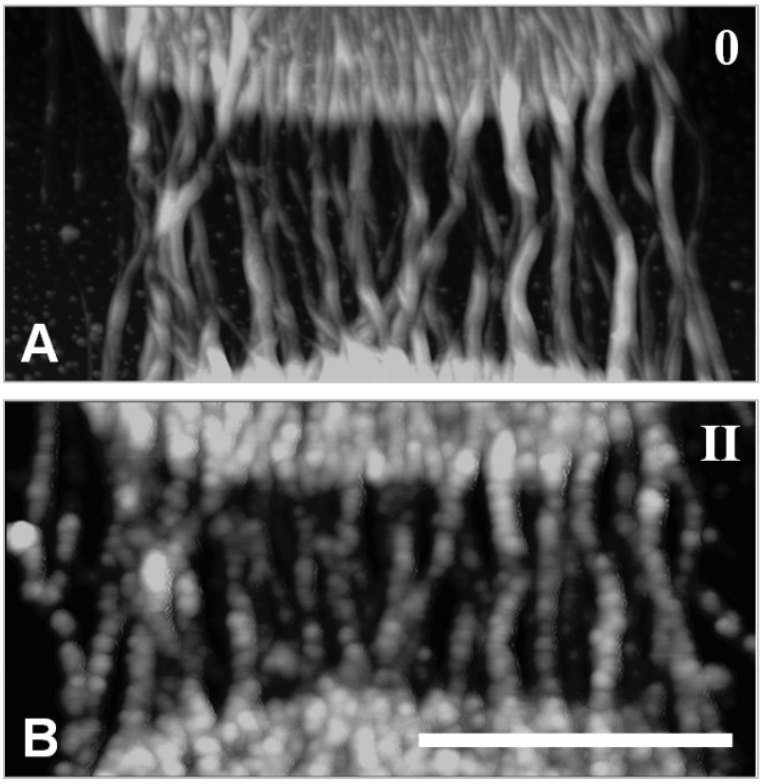

Figure S3: AFM topography images of a single CNT-FET (the same one as shown in Figure 4d in the paper [but enlarged] and Figure S4 in this ESI below) before (A, 0) and after (B, II) wafer-level decoration with gold nanoparticles. The scale bar in the image is 1 µm. (Source: T. Blaudeck, D. Adner et al., *Microelectronic Engineering* 2015, **137**, 135-140).

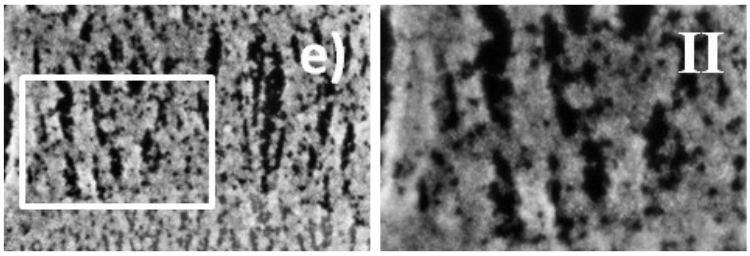

Figure S4: SEM images of the functionalized CNTs in CNT-FET structures at 100.000-fold (left) and 150.000-fold magnification of the same CNT-FET presented in Figure 4d in the paper and S3 in the ESI above). The scale bar is 100 nm. (Source: T. Blaudeck, D. Adner et al., *Microelectronic Engineering* 2015, **137**, 135-140).

B.2 Compositional (EDX) analysis of the Au-decorated CNT-FETs

Figure S5 holds a detailed EDX analysis of the CNT-FET shown in Figure 4d of this paper (same as Figure S3 and S4 in this ESI above).

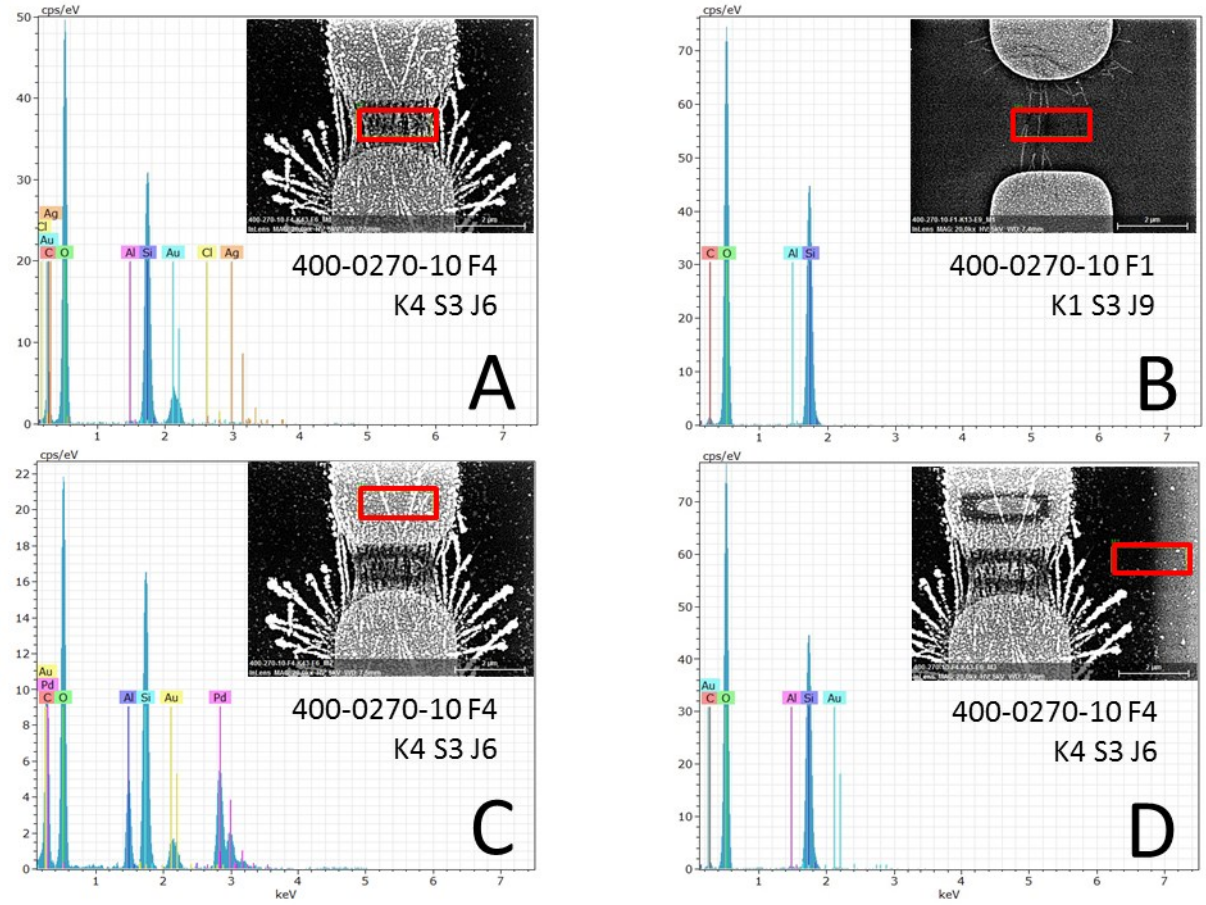

Figure S5: Energy-dispersive X-ray (EDX) spectra of semiconducting single-walled CNTs integrated between two Pd electrodes on a silicon wafer. (A) after decoration with gold nanoparticles and spectrum taken at an area of bridging CNTs (similar to Figure 4d in the paper and S4B in this ESI above); (B) without gold decoration (similar to Figure S3A in this ESI above); (C) same sample as (A) but spectrum taken at the Pd electrode; (D) same sample as (B) but spectrum taken aside of the bridging CNTs but still in a region where the microfluidic flow of the gold nanoparticle dispersion was applied. (Source: T. Blaudeck, D. Adner et al., *Microelectronic Engineering* 2015, **137**, 135-140).

C. Kataura plot

We obtained the theoretical Kataura plot from literature[2] as follows:

$$E_{ii}(p,d_t) = \alpha_p \frac{p}{d_t}\left[1 + 0.467\log\frac{0.812}{\frac{p}{d_t}}\right] + \beta_p \cos\frac{3\theta}{d_t^2},$$

where d_t is the SWCNT diameter and θ is the

SWCNT chiral angle, p = 1:8 for the optical transitions E_{11}^S, E_{22}^S, E_{11}^M, E_{33}^S, E_{44}^S, E_{22}^M, E_{55}^S, E_{66}^S respectively; fitting parameters with values are used: $\alpha_{p=1:3}$=1.074, $\alpha_{p\geq 4}$=1.133, as well as β for the lower (upper) transitions with values: β_p= -0.07(0.09), -0.18(0.14), -0.19(0.29), -0.33(0.49), -0.43(0.59), -0.6(0.57), -0.6(0.73), -0.65 (unknown) for p = 1:8. Raman shift of the radial breathing mode is calculated as: $\omega_{RBM} = \frac{227}{d_t}\sqrt{1+\frac{C}{d_t^2}}$, where C is the environmental coefficient set to 0.05.

Kataura plot was fitted with experimental data acquired with multiple laser lines (325, 476.2, 482.5, 488, 514.7, 530.9, 568.2, 632.8, 647.1, 676.4, 752.5 nm) according to procedure reported by Maultzsch *et al.* [1]. That is, the optical transition energy was adjusted by -0.08 eV to account for the preparation procedure of SWCNTs and their environment.

1. J. Maultzsch, H. Telg, S. Reich and C. Thomsen, *Physical Review B*, 2005, **72**, 205438.
2. Raman Spectroscopy in Graphene Related Systems Ado Jorio, Mildred S. Dresselhaus, Riichiro Saito, Gene Dresselhaus, ISBN: 978-3-527-40811-5, 368 pages, January 2011