# Wafer-Level Functionalization of Integrated Carbon Nanomaterials with Metal Nanoparticles

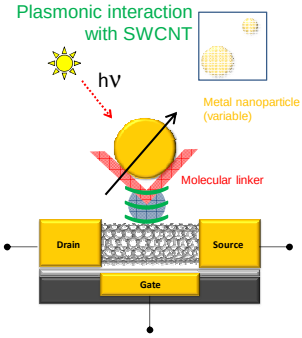

**Thomas Blaudeck[1], David Adner[2], Youwei Zhang[1,3], Sascha Hermann[1], Stefan E. Schulz[1,4], Ran Liu[3], Heinrich Lang[2] and Thomas Geßner[1,4]**

[1]Technische Universität Chemnitz, Center for Microtechnologies (ZfM), 09107 Chemnitz, Germany
[2]Technische Universität Chemnitz, Inorganic Chemistry, 09107 Chemnitz, Germany
[3]Fudan University, School of Microelectronics, Fudan, P. R. China
[4]Fraunhofer Institute for Electronic Nano Systems, 09126 Chemnitz, Germany


## Motivation

Semiconducting single-walled carbon nanotubes (s-SWCNTs) are a key material for nanometer-scale integrated sensors and actuators (for instance, MEMS/NEMS). For these applications, scalable technological solutions for the integration of the SWCNTs on wafer level are challenging. For sensoric applications, a suitable **chemical functionalization** of the SWCNTs keeping the electronic band structure intact is another key issue, likewise compatible to wafer processing.

In this contribution, we report on attempts towards SWCNTs that are functionalized with metallic nanoparticles on wafer level. The target application is a plasmonic sensor based on a SWCNT field effect transistor, with the gold nanoparticles expected to yield a tunability of the response properties.



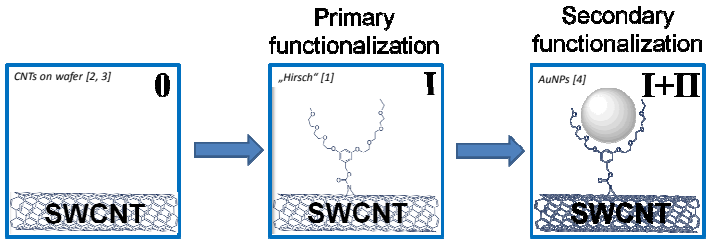

**Target application:**
*Optical sensor based on CNT-FET*

We employ a primary functionalization with ethylene glycol chains, inducing only few additional defects to the CNT. The functionalization is done via two approaches: liquid immersion of the wafer (**Approach 1**) and application of a microfluidic flow on the wafer (**Approach 2**). The results for SWCNTs are compared with graphene.

## Functionalization of Carbon Nanotubes

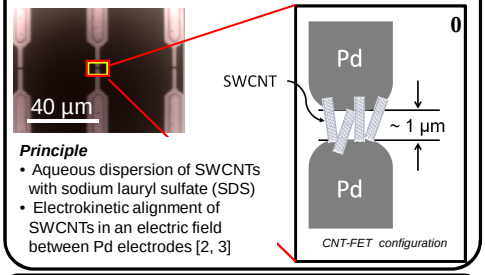
### Technological approach

- Protocols for primary functionalization of the SWCNTs are expanded from literature (Holzinger, Hirsch *et al.*) [1]
- The precursor molecules for primary functionalization of the SWCNTs are synthesized in a multi-step procedure, with the ethylene glycol chains designed towards an effective interaction with metal nanoparticles
- The primary functionalization of the SWCNTs (attachment of oxycarbonylnitrenes) is obtained by a thermally induced 1,3-dipolar cycloaddition of the SWCNTs directly on the wafer [2, 3]
- The secondary functionalization of the SWCNTs is done with gold nanoparticles synthesized according to published procedures developed previously [4]




## Wafer-Level Integration & Functionalization of Carbon Nanomaterials

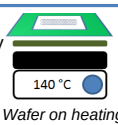
### Wafer-level deposition




***Principle***
- Aqueous dispersion of SWCNTs with sodium lauryl sulfate (SDS)
- Electrokinetic alignment of SWCNTs in an electric field between Pd electrodes [2, 3]

### Wafer-level functionalization

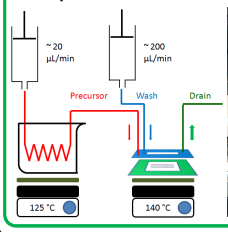
**Approach 1:**
Primary and secondary functionalization by liquid immersion of the wafer



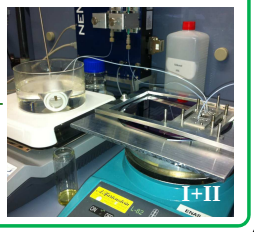

***Tool:*** *Wafer on heating plate*

**Approach 2**: Primary and secondary functionalization in microfluidic flow on the wafer

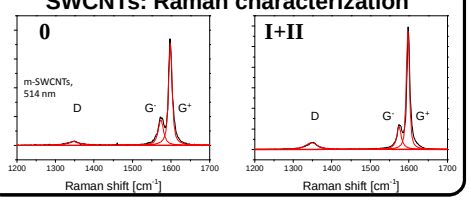
***Principle***



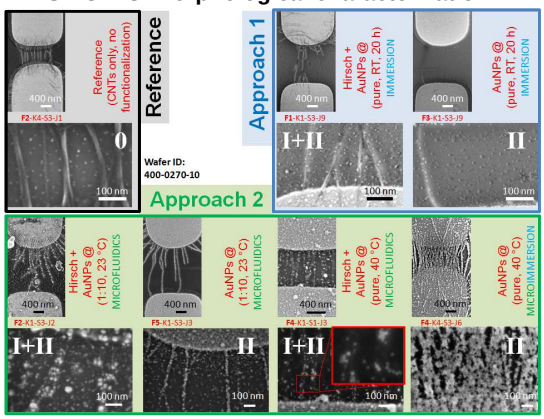

***Tool:*** Reactor on heated wafer



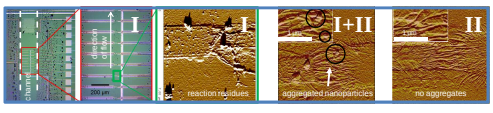

### SWCNTs: Raman characterization




### SWCNTs: Morphological characterization

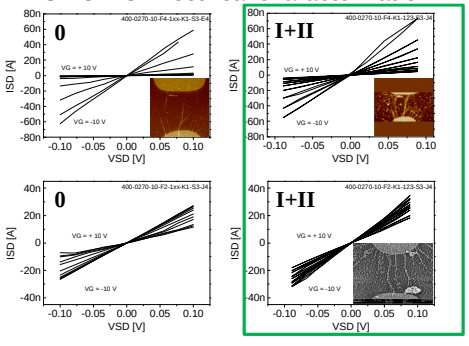



***SEM images*** *of several CNT-FET junctions after primary and/or secondary functionalization*



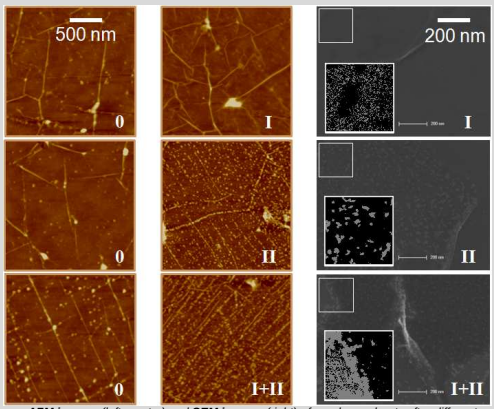

***Optical*** *microscope images of CNT-FET junctions after primary functionlization* — ***AFM image*** *of a CNT junction after primary functionalization* — ***... after*** *primary and secondary functionalization* — ***... after secondary without*** *primary functionalization*

### SWCNTs: Electrical characterization




***Current-voltage*** *characteristics of CNT-FET junction before and after functionalization*

### Graphene: Morphological characterization




***AFM images*** *(left, center) and* ***SEM images*** *(right) of graphene sheets after different combinations of primary (I) and/or secondary (II) functionalization. The inset in the SEM images represent transformations of the contrast image to identical greyscales.*

## Results

- For SWCNTs, a **successful adsorption** of nanoparticles in the presence of oxycarbonylnitrenes can be proven.
- The density of nanoparticles on the CNTs can be varied by **concentration** and **temperature** of the dispersion.
- After the functionalization process, the current-voltage characteristics of the CNT-FETs stay intact.
- For graphene, a successful adsorption of nanoparticles at the boundaries of the sheets can be observed both in presence and absence of oxycarbonylnitrenes. However, in the latter case, the aggregation of the particles is stronger.
- Raman spectra indicate that SWCNT sidewalls do not carry more defects as they show no raised D peak.

## Conclusions

- Electrokinetic **integration of carbon nanotubes** and **subsequent functionalization** with gold nanoparticles via oxycarbonylnitrenes **on wafer scale** is possible.
- The most promising results are obtained by a microfluidic approach.

## References


**[1]** M. Holzinger, J. Abraham, P. Whelan, R. Graupner, L. Ley, F. Hennrich, M. Kappes, A. Hirsch: "Functionalization of single-walled carbon nanotubes with (R-)oxycarbonyl nitrenes", *Journal of the American Chemical Society* **125**, 8566 (2003).
**[2]** H. Yu, S. Hermann, S. E. Schulz, T. Geßner, Z. Dong, W. J. Li, "Optimizing sonication parameters for dispersion of single-walled carbon nanotubes", *Chemical Physics* **408**, 11 (2012).
**[3]** R. D. Rodriguez, M. Toader, S. Hermann, E. Sheremet, S. Müller, O. D Gordan, H. Yu, S. E Schulz, M. Hietschold, D. R. T. Zahn: "Nanoscale optical and electrical characterization of horizontally aligned single-walled carbon nanotubes", *Nanoscale Research Letters* **7**, 682 (2012).
**[4]** A. Tuchscherer, D. Schaarschmidt, S. Schulze, M. Hietschold, H. Lang: "Gold Nanoparticles Generated by Thermolysis of "All-in-One" Gold(I) Carboxylate Complexes", *Dalton Transactions* **41**, 2738-2746 (2012).



**Contact**: Dr. Thomas Blaudeck
**E-mail**: thomas.blaudeck@zfm.tu-chemnitz.de
**Phone**: +49 (0) 371.531.35610

Chemnitz University of Technology
Center for Microtechnologies (ZfM)
Reichenhainer Str. 70
09126 Chemnitz, Germany



**Acknowledgements:** This work has been funded by the **Deutsche Forschungsgemeinschaft** (DFG) in the framework of the Research Unit FOR1713 „**Sensoric Micro and Nano Systems**" and the IRTG GRK1215 „**Materials and Concepts for Advanced Interconnects and Nanosystems**".