Interaction of Gold Nanoparticles with Wafer-level Integrated Carbon Nanotubes Probed by Raman Spectroscopy

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Introduction

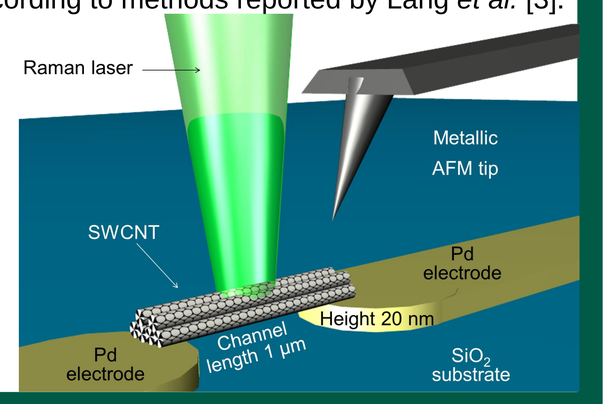
Single-walled carbon nanotubes (SWCNTs) hybrids with metal nanoparticles have received particular interest in science and technology as they are key building blocks for the realization of both miniaturized and high performance sensor devices. A critical step to reach technology maturity is **the integration in microelectronic systems** such as carbon-nanotube-based field-effect transistors (CNT-FETs). We have devoted our research to **wafer-level integration** and **wafer-level functionalization** of carbon nanotubes towards optical sensor systems with footprints of the sensitive element as small as a few μm^2.

The aim of this experimental study is the determination of the effects of gold nanoparticle decoration on the Raman spectra of a chiral mixture of SWCNTs integrated between Pd electrodes in a CNT-FET configuration, revealing the specific interactions.

Experimental Methods

Silicon wafers were structured by standard microelectronic processing comprising photolithography, etching, and deposition of metallic and dielectric layers. CNT-FET structures were prepared by **electrokinetic deposition** of semiconducting SWCNTs (Nanointegris, purity 99 %) between the structured Pd electrode fingers [1]. This method was rendered to wafer-level compatibility based on CNT dispersion protocols reported by Hermann *et al.* [2]. Au nanoparticles were synthesized according to methods reported by Lang *et al.* [3].

The characterization of CNT-FET structures was carried out with a Horiba Raman Spectrometer Labram HR800 with details described in [4]. A 100 × objective (N.A. 0.9), diffraction gratings of 600 l/mm and 2400 l/mm provide a spectral resolution of ~ 6.5 and 1.2 cm^{-1}, respectively. A solid state laser with 514.7 nm excitation wavelength was used as the Raman excitation.



Decoration of SWCNTs with gold nanoparticles: Effect on Raman spectra

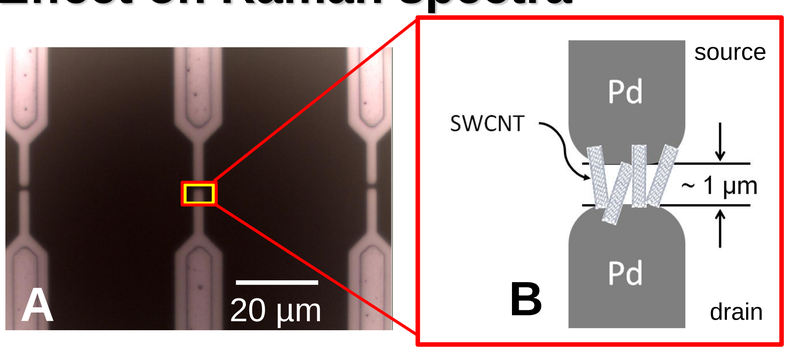


Figure 1. Optical microscope image of a palladium electrode structure (A) with a sketch of integrated SWCNTs.
(B) Scheme of the CNT-FET in back-gate configuration (top view). Atomic force microscopy images of a single CNT-FET before (C) and after (D) decoration of the SWCNTs with Au nanoparticles. This functionalization step was performed by a wafer-compatible microfluidic approach (see Poster DS 35.17).

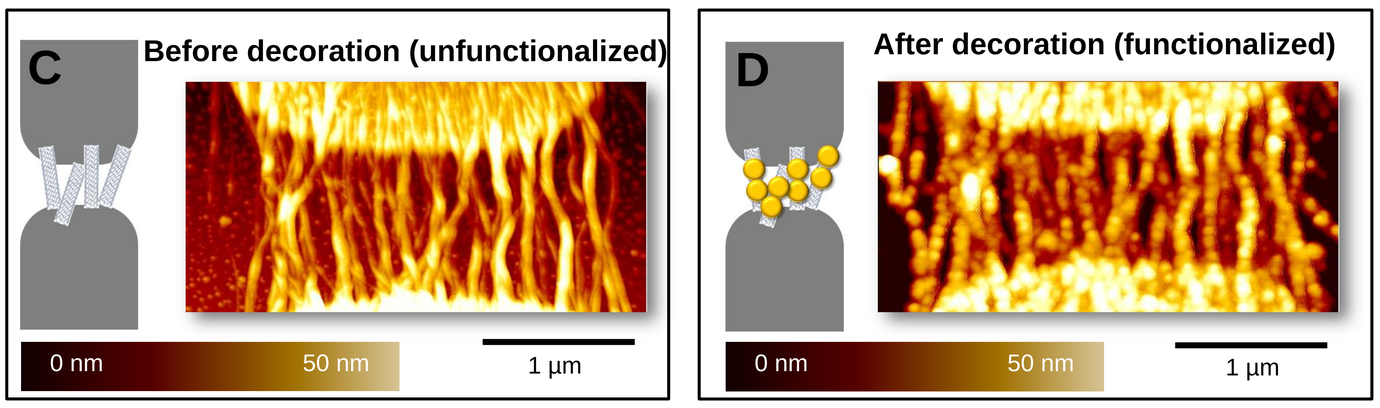
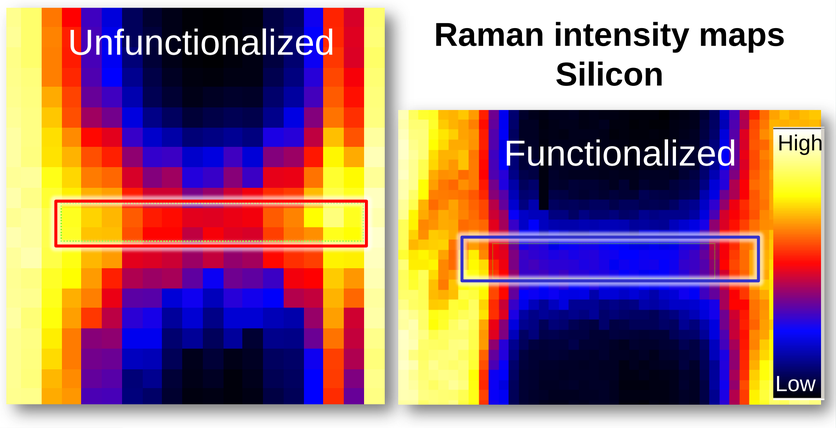
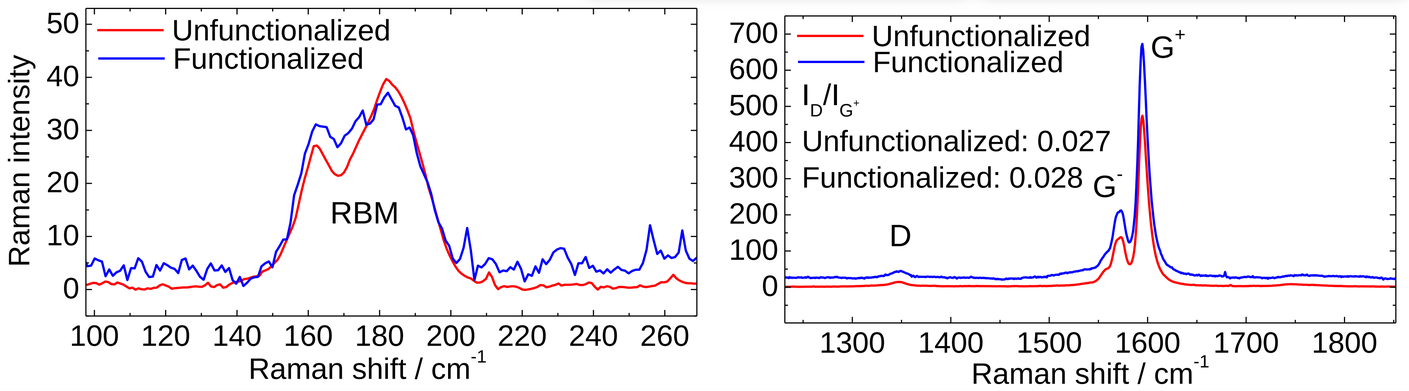


Figure 2. Raman spectra before and after functionalization averaged over the regions indicated – red line indicates spectra taken before functionalization and in blue line afterwards. The most apparent changes are taking place at the radial breathing mode where the small diameter tubes (higher frequency) are preferentially affected by functionalization. The compared spectra of D and G band region show no increased defect concentration after the functionalization procedure.





Kataura plot for CNT chirality determination

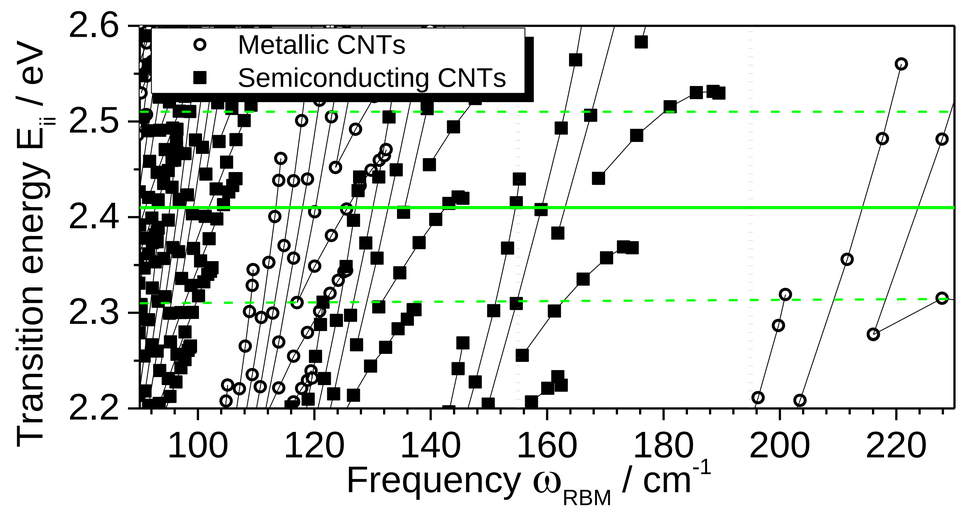


Figure 3. Kataura plot in the frequency range relevant for nanotube diameters expected in the CNT sample with measured RBM window as grey dotted vertical lines. Solid green line indicates excitation laser line used to study the samples with a resonance window indicated by green dashed lines.

Carbon nanotube diameters: RBM and G⁻ band cross-correlation

- The main peaks in RBM and G⁻ band were fitted and according to experimentally determined parameters, the diameters were calculated .

$$\omega_{RBM} = \frac{c_0}{d_t} + c_1 \qquad \omega_{G^-} = \frac{a_0}{d_t^2} + a_1$$

$c_0 = 215\ nm, c_1 = 18\ cm^{-1}$ [5] $\qquad a_0 = 47.7\ nm^2, a_1 = 1591\ cm^{-1}$ [6]

Table 1. Calculated carbon nanotube diameters from fitted experimental data (see Fig. 2). The diameters fitted for both RBM and G⁻ region are within 1.2 – 1.8 nm. Values before and after functionalization are unchanged, indicating that environment does not play a role a diameter evaluation and the experimentally determined equation is robust within the different environments.

Unfunctionalized				Functionalized			
ω_{RBM} / cm^{-1}	d_t / nm	ω_{G-} / cm^{-1}	d_t / nm	ω_{RBM} / cm^{-1}	d_t / nm	ω_{G-} / cm^{-1}	d_t / nm
162.1 ± 0.1	1.52	1556.5 ± 0.8	1.22	162.6 ± 0.1	1.52	1556.8 ± 0.4	1.23
174.5 ± 0.2	1.40	1567.4 ± 0.4	1.51	173.6 ± 0.2	1.41	1567.4 ± 0.2	1.52
182.4 ± 0.1	1.33	1573.5 ± 0.3	1.79	182.8 ± 0.2	1.33	1573.1 ± 0.2	1.78
190.1 ± 0.2	1.27			191.1 ± 0.3	1.26		

Summary

- Small diameter CNT are preferentially affected by the decoration process with Au nanoparticles while no significant increase in defect concentration was observed from the D/G intensity ratio.
- It is possible to achieve functionalized CNT-FET devices without degrading its electronic properties but preserving the CNT crystallinity and sp^2 nature.
- A selective attachment of Au nanoparticles to the CNT can be observed. The probable reasons (*e.g.* anisotropic cluster diffusion on CNT, interparticle coalescence, interactions between CNT-residual sulfides with Au) are currently under investigation.
- Decorated CNTs show a better contrast in the Raman mapping of silicon. This enhanced visibility might be ascribed to more effective light scattering in the case of present Au nanoparticles.

Acknowledgements

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