Carbon Nanotubes for Mechanical Sensor Applications

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Herein, the evolution of carbon nanotubes (CNTs) as functional material in nano- and microelectromechanical systems (N/MEMS) is featured. Introducing material morphologies for the CNTs in a homologue series (single CNTs—bundles, fibers, yarns—networks and thin films), different concepts for mechanical sensors based on the intrinsic and extrinsic properties of the CNT materials are introduced (piezoresistive effect, strain-induced band bending, charge tunneling). In a rigorous theoretical treatment, the limits of the achievable sensor performance (i.e., gauge factor) are derived and discussed in the context of applications. A careful literature survey shows that highest sensitivity is reached for devices exploiting the intrinsic transport properties of single CNTs. For reliability tests of such sensor systems made from nanomaterials and classical MEMS, the specimen-centered approach (SCA) is introduced to give viable insights into the structure property relationships and failure modes of CNT mechanical sensors. CNT actuation occurs on the macro-, micro-, and nanoscales via atomic force microscopy, electrostatic gating, integration in N/MEMS systems, or through substrate bending.

1. Introduction

Carbon nanotubes (CNTs) have emerged as a versatile material for a variety of sensor applications, especially mechanical sensors. Nanomorphology of the constituents plays a decisive role while quantifying sensor properties, e.g., mechanical sensing depends on the contact material, the quality, and composition of the CNT solid as well as the electrostatic environment. As systematic, comparative studies are rare, this article attempts to systematically correlate mechanical sensor performance (in terms of gauge factor) with morphology of the CNT constituents and their immediate environment. It derives a theoretical concept for CNT-based mechanical sensors, organizes reports from experimental, theoretical, and numerical literature, and reveals correlations between the sensor sensitivity and morphology.

The fact that reported gauge factors of devices based on single-walled CNTs (swCNTs) are significantly above theoretical predictions for the intrinsic CNT gauge factor requires to rule out possible, fundamental issues. First, the traditional definition of the gauge factor turns out to be strongly strain dependent for CNTs. Therefore, a strain-independent measure must be found, e.g., the differential gauge factor in the limit of low strain (introduced in Section 2.3). This requires a careful analysis of existing literature data for differential gauge factors. Second, the picture of intrinsic CNT piezoresistance has to be re-evaluated for CNT devices, and CNT contact physics has to be taken into consideration. Third, the CNT properties as a surface material depend on its environment. Therefore, the CNT testing environments and conditions need to be elucidated. The superimposed goal of all this is to provide a sound picture of CNT piezoresistance for single CNT devices.

As strained CNT devices also consist of macroscopic CNT networks, thin films, or yarns, these material classes and the
physical origin of their strain response are also discussed within this work. The different CNT morphologies and their production have to be revisited to provide an overview over existing CNT material classes.

2. CNT Strain Sensor Technology

2.1. Taxonomy on CNT Solid Materials

As shown in the upper row of Figure 1, CNT solids can span a range of complex morphologies from bulk composites and intricate networks of CNTs, down to single, well-debundled quasi-1D CNTs, shaping the particular applicability of the material. The resulting solid depends on the fabrication process of the CNTs, i.e., growth (arc discharge, laser vaporization, catalytic decomposition of hydrocarbons and chemical vapor deposition (CVD), low-pressure combustion, electrolysis and others; see the review by Kingston and Simard for details[46]) and the particular deposition of the grown material on substrates, e.g., from the liquid phase (cf. further below).

Electrospray methods were suggested to push the production of long, straight, and single fibers for mechanical applications.[3] However, the named conventional production methods have so far been unprecedented when it comes to production of nanomaterials with defined properties for new solutions in microelectronics with nanoscopic building blocks.

Schematic cross sections of the respective CNT solids are shown in the center row of Figure 1. They span a variety from single CNTs (exposing almost solely the intrinsic electronic and mechanical properties of the CNT) via aligned individual CNTs (with a minimum of extrinsic bulk effects imposed by their neighborhood) and CNT bundles (or ropes, fibers, yarns) to disordered CNT networks (with an increasing amount of tunnel contacts dominating the bulk CNT conductance) or CNT thin films. The latter category is characterized in first order by the properties of the surrounding matrix, whereas the nanoscopic nature of the CNT constituents in the matrix naturally has significant influence on the bulk properties of the material. The tendency of CNTs to aggregate and form superstructures was already reported by Smalley and coworkers, who obtained elongated solids (called “ropes”) of 100–500 individual swCNTs arranged in quasi-1D triangular arrays with hexagonal lattice constants[6] as indicated for CNT bundles in Figure 1. Current developments in nanoelectronic technology comprise the integration of individualized CNTs in electronic device platforms. Examples are attempts of CNT-based logic circuits,[7–10] sub-microscale optoelectronic devices comprising photodetectors, emitters, and plasmonic transducers,[11–21] nanoelectronic sensors for chemical substances,[22–26] as well as plasmonically assisted detectors of biological molecules.[27,28]

Furthermore, CNTs act as nanoscale transducers or actuators in nano- and microelectromechanical systems (N/MEMS).[28–34] Deposition of CNTs from suspended dispersion in the liquid phase, either evaporation assisted[35,36] or electrokinetically supported through external electrical fields by dielectrophoresis (DEP),[30,31,33,34,37–39] has proven appropriate for the fabrication of CNT-based films, components, and devices. Here, a prerequisite for device fabrication is to effectively debundle CNTs, which goes along with length[13] and chiral[40] separation of the constituents of dispersion. In principle, CNT aggregation and bundle formation in the final state of the device inhibit the performance surplus expected from the usage of individualized CNTs as nanoelectronic components.

In general, CNTs dispersed in a polar solvent like water can be treated as colloidal systems, for which coagulation (i.e., the aggregate formation of its constituents) is driven by the relative interplay between attractive van der Waals interactions and
Furthermore, Rodriguez and coworkers found Morphologies (own artwork) of different CNT solids from single CNTs via CNT bundles (or ropes, fibers, yarns) to CNT networks and thin films in a homologue series of their increasingly complex order: top view (upper row), cross section (center row), and estimated prevalence of intrinsic versus extrinsic sensor effects (lower row). Cross sections and respective terminology according to Zhang et al.,[1] Tsareva et al.,[2] and Muris et al.[3]

In Figure 1, the surface potential,[41] Raman measurements together with aggregated nanoparticles,[20] and, for predictions of the molecular structure, molecular dynamics simulations.[42,43] Khan et al. also suggest time-resolved dynamic light scattering and molecular dynamics simulations to study the aggregation kinetics of oxidized swCNTs as a function of the salt concentration of the surrounding solvent and tube chirality. They found that the critical coagulation concentration of monovalent (NaCl) and divalent (CaCl$_2$) ions decreases by a factor of 7 and 5, respectively, when increasing the tube diameter from 7.6 Å (6,5-swCNTs) to 8.9 Å (7,6-swCNTs).[43] Furthermore, Rodriguez and coworkers found that smaller tubes prefer to form the exohedral surface of the bundle, if it is formed by a mixture of CNTs with different chirality and radii.[20]

For a description of the structural organization of as-produced CNT bundles, Tsareva et al. suggested swCNT bundles as quasi-1D structures with arrays of four different possible adsorption sites.[2] In relation to the earlier models by Williams and Eklund[44] and Muris et al.[3] these authors discriminate between the exohedral surface with external grooves that separate two adjacent outer tubes, the endohedral (or inner) channels of the tubes, and interstitial channels (cf. Figure 1). Already in the early 1990s, Tersoff and Ruoff calculated the condensed-phase morphology of CNTs and predicted the structural properties switch between two regimes with qualitatively different morphological properties, as their tube diameter varies. While tubes with a diameter of 1 nm and less keep the shape of rigid cylinders, tubes with a diameter of 2.5 nm and above undergo a flattening against each other. On account of the van der Waals forces, they form a rigid honeycomb structure.[45] Meanwhile, this hexagonalization was found also for other types of nanotubes, such as inorganic imogolites.[46] Currently, the topic of organic nanotubes made from π-conjugated molecular systems different to CNTs (e.g., porphyrins and other tetrapyrrrole constituents involved in photosynthesis) has emerged in applied research, as these superstructures show interesting relationships between their structure and their mechanical, optical, and electronic properties and a high degree of biocompatibility.[47]

2.2. Intrinsic and Extrinsic CNT Sensor Effects

All CNT solids are generally suited for mechanical strain sensing on the nanoscale. CNT sensing principles, with respect to the properties of the individual CNT, can be intrinsic, extrinsic, or any combination of both. The tentative prevalence of intrinsic versus extrinsic electronic and mechanic effects in materials of the different CNT morphologies is indicated in the lower row of Figure 1.

Intrinsic effects are related to the change in the electronic bands of the individual CNT (or the interactions of its bands) with respect to external perturbation, such as electronic and optical excitations[48–50] and strain.[19,51–55] In Figure 1 (upper row), this is given for single and aligned CNTs.

Extrinsic sensing principles are related to the interaction of CNTs with one another (indicated by the cross sections in Figure 1) and/or their particular environment (indicated by the green solid area around). This viewpoint includes primarily the network effects imposed by the tunnel contacts alongside the percolation system of the CNT solid (bundle or network).[56] The concept of CNT thin films extends this picture to interactions of the CNT network with its surrounding matrix[57] (indicated by a color change in the surrounding from green for CNT networks to gray for CNT films in Figure 1).
A special case is generated, when CNT properties are tuned electronically by doping or gating: this is a priori neither uniquely extrinsic nor intrinsic. Gating or doping changes the occupations of bands in a CNT and with this, the Fermi level. The shift of the bands with respect to each other is usually small and cannot be resolved experimentally. Thus, we label electronic tuning as an extrinsic effect.

2.3. Absolute and Relative Gauge Factor

The gauge factor $\beta_{GF}$ is the measure of the strain dependence of CNT devices for all cases, intrinsic as well as extrinsic strain response. It is defined as the relative change in the resistance $R$ per relative strain $\varepsilon$

$$\beta_{GF} = \frac{R(\varepsilon) - R_0}{R_0 \varepsilon} = \frac{\Delta R(\varepsilon)}{R_0 \varepsilon}$$  \hspace{1cm} (1)

where $R_0$ denotes the resistance in the relaxed state. This gauge factor is strain independent as long as change in the resistance $\Delta R(\varepsilon)$ is linear with strain—which is approximately the case for many bulk materials. However, in the case of low-dimensional materials, especially CNTs and CNT composites, the response is often nonlinear—as discussed in Section 3.1. Therefore, the more universal, strain-independent measure for a given material is the gauge factor in the limit of small strain, $\beta_{GF}$

$$\beta_{GF} = \lim_{\varepsilon \to 0} \beta_{GF} = \frac{1}{R_0} \frac{\partial R(\varepsilon)}{\partial \varepsilon} = \frac{1}{G_0} \frac{\partial G(\varepsilon)}{\partial \varepsilon}$$  \hspace{1cm} (2)

where $G = \frac{1}{R}$ and $G_0 = \frac{1}{R_0}$ denote the conductance of the material in the relaxed and the strained state, respectively. It becomes visible that $\beta_{GF} = \beta_{GF}$ for $\Delta R(\varepsilon) \sim \varepsilon$ (e.g., conventional bulk materials, such as doped silicon $^{[58-60]}$).

Finally, many references report on $\beta_{GF}$ for CNTs or composites, others report on $\beta_{GF}$, which makes it necessary to homogenize those values and to convert between them. The reason is the specific focus of the individual publication. While $\beta_{GF}$ is more practical to compare fabricated devices (often designed for a specific strain $\varepsilon$), $\beta_{GF}$ is useful to compare the material response. As the focus of this article is put on the sensor response of the particular material (including morphology), we stick to the relative gauge factor $\beta_{GF}$ in the following section.

2.4. Testing Methods of CNT Sensors

For the application of CNTs as strain sensors, the correct determination of the gauge or strain factor of the used CNTs is of great importance. Table 1, 2 and Figure 5 give an overview on published gauge factors originating from different setups. Values documented in the literature span from 0 to 2000 without any preference for smaller or larger values. While covering such a wide range, the question regarding test procedures, sample preparation, and reproducibility arises. Figure 2 shows common CNT testing principles from the publications cited in Table 1, 2, and Figure 5. They can be roughly clustered into microscopic and macroscopic approaches with regard to the experimental setup.

Microscopic approaches typically test single or small networks of swCNTs or multiwalled (mwCNTs) based on custom-designed MEMS devices. These range from gravity and weight-utilizing bending devices, $^{[94-100]}$ over membrane-based pressure sensors $^{[29,31,64]}$ with various forms of actuation, to cantilever structures being actuated by an AFM tip $^{[62,63,66-67]}$. Such cantilever actuation can be used to determine the maximum pull-out force of CNTs from the metal contact for microscopic devices. $^{[35,107-109]}$

### Table 1. Overview of CNT gauge factors in literature: Experimental results for CNT N/MEMS devices are presented in section I of the table, their theory in section II. Abbreviations: semiconducting (sc), semimetallic (sm), double-walled CNT (dwCNT).

| Gauge factor as reported | $\beta_{GF}$ from fit \( \times \text{recalculated (this work)} \) | CNT material | Author/year |
|--------------------------|---------------------------------------------------|--------------|-------------|
| I                        |                                                   |              |             |
| 1800                     | 150\(n\)                                          | Single sm swCNT | Tombler et al., 2000 $^{[61]}$ |
| n.a.                     | 40–60, 150                                         | Single sc swCNTs | Cao et al., 2003 $^{[32]}$ |
| 600–1000                 | 440 ± 20\(n\), 600 ± 20\(n\)                      | Single sm swCNTs | Cao et al., 2003 $^{[32]}$ |
| n.a.                     | 6, 213                                            | Single sc/sm swCNT | Minot et al., 2003 $^{[33]}$ |
| 30–865                   | 250–640\(n\)                                      | Single sc/sm swCNTs | Grow et al., 2005 $^{[34]}$ |
| 190                      | n.a.                                              | \(\approx\)10 swCNTs in parallel | Maune and Bockrath, 2006 $^{[65]}$ |
| 0–2000                   | 0–740\(n\)                                        | Single sm swCNT | Stamper et al., 2006, 2007 $^{[94,97]}$ |
| n.a.                     | 78–140                                            | Aligned swCNTs | Tong et al., 2007 $^{[15]}$ |
| 210                      | 190 ± 10\(n\)                                     | Aligned swCNTs | Hierold et al., 2008 $^{[29]}$ |
| n.a.                     | 75 ± 5                                            | Aligned sc swCNTs | Cullinan et al., 2010 $^{[39]}$ |
| n.a.                     | 10–450                                            | Single swCNT | Helbling et al., 2011 $^{[31]}$ |
| 20–70                    | 165 ± 13\(n\)                                     | Single sc dwCNT | Muoth et al., 2013 $^{[32]}$ |
| 0–600                    | 0–410                                             | Single sc swCNT | Böttger et al., 2019 $^{[34]}$ |
| II                       |                                                   |              |             |
| n.a.                     | 0–280                                             | Single swCNT (theory) | Cullinan et al., 2010 $^{[39]}$ |
| n.a.                     | 0–340                                             | Single swCNT (theory) | Wagner et al., 2012 & 2016 $^{[33,34]}$ |
This work is especially useful to determine the maximum strain that can be achieved by N/MEMS-actuated CNTs as a function of contact material and functional CNT surface groups. An exception to be noted is the approach described by Hierold and coworkers. Both publications feature custom-designed MEMS devices driven by (thermal) actuators capable of testing single or multiple CNTs in parallel. In most cases, CVD is used to produce the CNTs, which are then mechanically transferred to their positions in the testing devices. Only a few references explicitly mention DEP.

Macroscopic approaches are not capable of testing structures of single CNTs; instead, they focus on the creation of macroscopic structures as films, dog bones, or yarns which are tested using macroscopic tensile testing devices. Besides this, substrate bending (as shown in Figure 2) and three- or four-point bending setups are discussed as alternatives. Besides such classical approaches, studies are presented in which CNT compounds are directly attached to the human body to sense the action of knees, fingers, and facial muscles—which also strains or bends the substrate. Films and foils are fabricated, e.g., using spraying of CNT compounds on polydimethylsiloxane or polyethylene terephthalate, coating rubber by hand, by drying CNTs in suspension, or by dispensing CNTs on carrier foils. Dog bones are created by embedding CNTs in polymers based on polysulfone, polyurethane, polyvinylidene fluoride, poly(methyl methacrylate), polyimide, or epoxy to name only some, which are then cut into appropriate shapes and characterized.

### Table 2. Overview of CNT gauge factors in literature: Experimental results on CNT bundles, yarns, fibers and ropes, networks, and films in section III, and the respective simulations in section IV. Abbreviations: double-walled CNT (dwCNT).

| Gauge factor as reported | CNT material | Author/year |
|--------------------------|--------------|-------------|
| III                      |              |             |
| 125                      | mwCNT film (doped) | Wan-Lu et al., 2003 [84] |
| 65                       | mwCNT film (undoped) | Wan-Lu et al., 2003 [84] |
| n.a.                     | mwCNT film | Maune and Bockrath, 2006 [85] |
| 0.89                     | mwCNT network in polyimide | Zhang et al., 2007 [89] |
| 15                       | mwCNT network in PMMA | Pham et al., 2008 [79] |
| n.a.                     | mwCNT network in epoxy | Hu et al., 2008 [77] |
| 0.5                      | CNT yarn | Zhao et al., 2010 [72] |
| n.a.                     | mwCNT polymer composite | Alamusi et al., 2011 [76] |
| 0.7 ± 0.18               | mwCNT/polymer composite films | Oliva-Aviles et al., 2011 [73] |
| 0.06–0.82                | mwCNT network in IPA | Yamada et al., 2011 [74] |
| 4.52                     | Vertically aligned CNT forest | Bzoul et al., 2012 [78] |
| 0.99                     | mwCNT network in elastomer | Cohen et al., 2012 [75] |
| 1–6.2                    | swCNT/poly(vinylidene fluoride) composite | Ferreira et al., 2012 [77] |
| 5–75                     | mwCNT/PU composite | Slobodian et al., 2012 [78] |
| 100                      | sw/dwCNT film (transparent) | Cai et al., 2013 [79] |
| 16                       | mwCNT buckypaper | DeGraff et al., 2017 [80] |
| 5                        | mwCNT film | Luo et al., 2013 [81] |
| 2.62, 6.2                | mwCNT/PCc composite (not aligned) | Parmar et al., 2013 [82] |
| 3.65                     | mwCNT/PCc composite (aligned) | Parmar et al., 2013 [82] |
| 5–80                     | mwCNT flakes in rubber | Tadakaluru et al., 2014 [83] |
| 20, 40                   | mwCNT network in epoxy, polyimide | Li et al., 2014 [84] |
| 1.1, 2.4                 | mwCNT ecoflex composite | Amjadi et al., 2015 [85] |
| 62                       | PU-PEDOT:PSS/swCNT/PU-PEDOT:PSS | Roh et al., 2015 [86] |
| 47, 64                   | mwCNT fibers on flexible substrate | Ryu et al., 2015 [87] |
| 2.5–16                   | Polycarbonate/mwCNT fibers | Bautista-Quijano et al., 2016 [88] |
| 10.5                     | Aligned mwCNT/elastomer | Suzuki et al., 2016 [89] |
| 0.977–3.21               | mwCNTs/epoxy composite | Sanli et al., 2016 [77] |
| 0.15                     | mwCNT yarn | Nguyen et al., 2017 [90] |
| n.a.                     | mwCNTs/epoxy composite | Tong et al., 2017 [91] |
| 20–120                   | Fe-filled CNTs on (Al) foil | Yang et al., 2017 [92] |
| IV                       | CNT network (simulations) | Hu et al., 2008 [77] |
| 0.33–0.61                | CNT network (simulations) | Rahman et al., 2012 [93] |
Finally, yarns are spun, e.g., using manually processed CNT arrays,\cite{72} dry-spinning processes,\cite{87,89} by piston spinning of CNT-polycarbonate yarns,\cite{88} or by processing CNT forests grown on a Si wafer.\cite{90}

The large deviations in the measurements of the gauge factor shown in Table 1, 2, and Figure 5 in combination with the wide field of testing methods collected here clearly emphasize a general challenge while testing samples on a micro- or nanoscopic scale. The steps undertaken to prepare the tested samples influence the specimen itself in a massive way so that a reliable judgment of the specimen in question does not seem valid anymore. In the light of this fact, the authors want to emphasize the importance of a specimen-centered approach (SCA). Such an approach addresses the issue that nanofunctional elements cannot be embedded, clamped, or fixed by other means without sacrificing on the reproducibility, integrity, or meaningfulness of the results. In the reviewed literature, only Hierold and coworkers\cite{29} describe the usage of SCA without explicitly mentioning it. Acknowledging this situation, the authors have put forward the SCA in earlier publications with the aim of conceptualizing and building block-based N/MEMS test stages\cite{111,112} as well as samples mounted by bottom-up self-assembly processes, as, for example, DEP.\cite{113,114}

In contrast to classical approaches, the SCA entails that the loading mechanism or stage has to emerge around and maybe even after the nanofunctional element to be tested is assembled. This implies that the processes required to create a loading stage have to be compatible with the process flow of heterogeneous integration of nanofunctional elements. Bonding and deep reactive ion etching\cite{115} in combination with multilayer silicon on insulator wafers has proven itself as the versatile method of choice.\cite{116} A given test stage comprises a capacitive displacement sensor, a thermal actuator,\cite{113} and a piezoresistive force sensor.\cite{112} The building blocks and test stages have been successfully applied to various test environments as, e.g., the vacuum chamber of a TEM.\cite{117}

2.5. CNT Strain Sensor and Actuator Applications

From the testing methods specified in the aforementioned section, there are different possibilities for the application of CNT mechanical sensors.

N/MEMS-based sensors can be used as force or acceleration sensors. These are based on the intrinsic (electronic) piezoresistive behavior\cite{19,21–25} and can be read out electronically. The CNTs are applied to increase the signal-to-noise ratio of classical MEMS, which are traditionally read out capacitively. There are also different attempts to measure the effect of strain on the optical transitions of a CNT\cite{118–121}—followed by theoretical predictions of the strain dependence of optical transitions.\cite{49,50} However, these devices are technologically challenging.\cite{118,119}

In a similar way, CNT ropes can serve as electronic force sensors,\cite{6} whereas CNT films are used as strain gauges to sense the movement of a piece of human skin or the body.\cite{78,79,86,89} Here, the morphology of the particular CNT solid governs the possibilities to intentionally alter the electronic properties of the CNT material by materials engineering (e.g., covalent and noncovalent functionalization of CNT sidewalls in external grooves\cite{19–21}) or in the context of sensoric function (e.g., adsorption of gas molecules in interstitial channels, cf. the cross section of the CNT bundle in Figure 1). Another application of the vibrational properties of CNTs are molecular gas sensors in which the mechanical response of a suspended CNT is monitored electronically or optically within a bridge (“clamped-clamped”)\cite{96,98,99,101,122,102,123} or cantilever (“fixed-free”)\cite{94,95,97–99,101–103,122,123,106} setup configuration (see Figure 2). In this sensor concept, in addition to purely electronic detection concepts based on Schottky barrier (SB) modulation at the CNT–metal interface\cite{100} or a local gate field perturbation within functionalized CNT transistor channels,\cite{104,105} the fundamental frequency of a CNT (usually a few GHz)\cite{106} is detuned (usually a few kHz)\cite{106} when gas molecules (from mass 7 zg down to 7 yg)\cite{106} or even single gold
atoms (1.66 yg) attach to it. Actuation of the resonator can be performed capacitively or piezoresistively. The amount of detuning can be used to calculate the mass of the molecule and detect the number of attached molecules or their molecular weight, if the number of attached molecules is known. The mass precision is sufficient to discriminate between single gas molecules (e.g., NH₃) and even isotopes. However, as the specific performance of a CNT resonator critically depends on the elementary properties of the used CNT (chirality, length, presence of preloaded surface-functional groups), all individual devices have to be pretested and precalibrated individually. A further, prominent application of a similar CNT device as an actuator is the swCNT radio which uses the fact that the mechanical resonance frequency of a CNT can be in the range of radio frequency.

There are also different kinds of pressure sensors available. One class of such devices is based on microscopic components in which CNTs are suspended between metal contacts at the edge of a membrane. When exposed to pressure, the membrane is deflected and the CNTs are strained, inducing a (differential) electronic signal. Macroscopic CNT pressure sensors are based on CNT films working as membranes and being exposed to a pressure difference. Such CNT-based pressure sensors cannot only sense gas pressure differences, but can also be used for gait analysis in human locomotion, envisaging, e.g., mapping of mechanical forces inside or on shoes.

3. CNT Strain Sensor Description

This section reviews CNTs working as strain sensors. The conductance of single CNTs and the conductivity of CNT superstructures are related with the respective gauge factors. Section 3.1 and 3.2 outline the fundamentals of CNT sensor technology considering both microscopic and macroscopic components. Section 3.3 reviews recent strain sensor applications. Figure 5 homogenizes and summarizes the findings of intrinsic and extrinsic strain response for many CNT sensors and relates the findings to the theoretical models presented in this section. As a side effect, the general performance of intrinsic and extrinsic CNT sensors is compared.

3.1. Intrinsic Sensor Response

The intrinsic CNT response is based on the change in the bandgap ΔEₘ with strain ε and torsion γ (where γ = 0 from now on).

\[ \Delta E_m(\varepsilon) = sgn(2p + 1)3\hbar(1 + \nu)[\varepsilon \cos(\theta) + \gamma \sin(\theta)] \]
\[ \equiv \beta \varepsilon \equiv \pm 150 \text{ meV} \cdot \varepsilon / \% \cdot \cos(\theta) \] (3)

p is a value constructed from the chiral indices n,m of CNTs and determines the sign of the bandgap change, \( \hbar = 2.66 \text{ eV} \) is the tight binding parameter of graphene π orbitals, and \( \nu = 0.2 \) is the CNT Poisson ratio. The short-hand coefficient \( \beta = \Delta E_m(\varepsilon) / \varepsilon \) can be considered as a CNT-specific prefactor.

The bandgap impacts the CNT conductance in two ways. Depending on the chosen device, the contact between the CNT and the metal can be either Ohmic or Schottky like. In any case, the SBs for electrons (Φₐ) and holes (Φₚ) change with strain and contribute to the thermionic conductance \( G_{th} \).

\[ G_{th}(\varepsilon) = \frac{4e^2}{h} \sum_{n,p} \gamma e^\frac{\Phi_{n,n}}{\Delta E_m} \sim G_{th}(0) \cdot \left[ e^{e^\frac{\Phi_{n,n}}{2\Delta E_m}} + e^{\left(1 - e^\frac{\Phi_{n,n}}{2\Delta E_m}\right)} \right] \] (4)

where \( \varepsilon \) is the elementary charge, \( h \) is Planck’s constant, \( k_B \) is Boltzmann’s constant, and \( T \) is temperature. The condition \( \Phi_n + \Phi_p = E_C \) is constrained. The coefficient \( \alpha \) depends on whether any of the bands or the Fermi level (the middle between the conduction and valence band) is fixed on strain—as shown in Figure 3. Consequently, \( 0.0 < \alpha < 1.0 \), whereas \( \alpha \) is specific for a given CNT contact material. The thermionic differential gauge factor \( \beta_{GF,th} \) can be identified by the exponent \( \beta \), which is, consequently, independent of \( \alpha \).

If the electrostatic force \( F \) at the contact, which corresponds to the gradient of the electrostatic potential \( F = \frac{d\phi}{dx} \), is significant, tunneling occurs. Tunneling is strain dependent and contributes to the total conductance by

\[ G_{tun} = \frac{4e^2}{h} e^{-\frac{\gamma \Phi_{n,n}}{2\Delta E_m}} \sim G_{tun}(0) \cdot e^{-\beta \Phi_{n,n}} \] (5)

Mostly, only one sort of carriers (p or n) dominantly contributes to the tunneling current—therefore, \( \Phi \) may be \( \Phi_p \) or \( \Phi_n \). Here, \( m^* \) is the effective mass of this carrier, which is also strain dependent: \( m^*(\varepsilon) \approx \varepsilon \). The respective tunneling gauge factor \( \beta_{GF,tun} = 2\beta_{tun} \approx F^{-1} \). Measurement results usually contain tunneling and thermionic effects, such that the total conductance \( G \) is \( G = G_{tun} + G_{th} \). This results in the total, differential gauge factor as the conductance-weighted average between the individual gauge factors

\[ \beta_{GF} = \frac{G_{tun}}{G} \beta_{GF,tun} + \frac{G_{th}}{G} \beta_{GF,th} \]
\[ = \frac{G_{tun}}{G} \beta + \frac{G_{th}}{G} 2\beta_{tun} \] (6)

As mentioned earlier, literature reports on \( \beta_{GF} \) and \( \beta_{GF,tun} \) as well. To homogenize the data in Figure 5, the limit of low strain is extracted from literature data, where \( \beta_{GF} \) is given.

3.2. CNT Network Response

For the CNT networks, the total conductance can be calculated by network simulations of the electrostatic potential as schematically shown in Figure 4. Basically, there are two main parameters that influence the conductance of the CNT network beyond connectivity as a topological factor: the conductance of the CNT junction \( G_{tun} \) and the intrinsic conductance of the CNT, which is equal to \( G_{th} \) from Equation (4). As the conductance of the CNTs in the network should be maximized, mwCNTs are usually chosen (see Table 1 and 2), where \( \Phi_{p,n} = 0 \) for \( N \) metallic shells—and thus, \( G_{th} = 4e^2 / n/h \).

The contact resistance of the mwCNT junction, which is a tunneling resistance, depends on the contact distance \( d \), the contact area \( A \), and the tunneling barrier height \( \lambda \) in the limit of weak electrostatic forces \( F \).

\[ R_{tun} = G_{tun}^{-1} = \frac{\lambda^2 d}{A e^2 \sqrt{2m^* \lambda}} \exp \left( \frac{4\pi d}{\hbar} \sqrt{2m^* \lambda} \right) \] (7)
The contact distance between the nanotubes changes linearly with strain $\epsilon$, as long as the strain direction is parallel to the shortest CNT–CNT distance: $d(\epsilon) = d_0(1 + \epsilon)$. (The angle between the strain direction and the CNT–CNT contact would lead to an effective strain rate $\epsilon^* = \epsilon \cos \theta$. In a disordered network, $\epsilon^* = \epsilon(\cos \theta) = \epsilon/2$.) $d_0$ is the CNT–CNT distance in the unstrained material.

In contrast to Section 3.1, only little (or no) strain is transferred to the CNT. (If the bonds between the host material and the CNT were covalent, strain could be transferred to the CNT; but also, its electronic properties would be disturbed.) Even if that would be the case, the conductance of mwCNTs is most likely strain independent: strain is only transferred to the outer shell, as the tubes will slip due to the relatively weak van der Waals forces between them. Furthermore, the bandgap of metallic zigzag tubes ($\theta = 30^\circ$) is strain independent and this (presumably large) fraction of metallic CNTs would not change its conductance.

In the limit of a single CNT–CNT junction, the gauge factor is (with $B = 4\pi\sqrt{2m^*\lambda}/\hbar$)

$$\beta_{GF,jun} = (1 + B d_0(1 + \epsilon))\exp(B d_0 \epsilon) + \frac{\epsilon - 0}{1 + B d_0}$$

(8)

Thus, the piezoresistivity of a single junction depends on the electronic configuration of the CNT and the host material by two parameters: $\sqrt{2m^*\lambda}$ (as a single, effective parameter) and the distance $d_0$ of the tubes—which is related to the tube density or CNT volume fraction. Furthermore, this means that the conductance $G$ and the gauge factor $\beta_{GF,jun}$ are interrelated.

A network of conductors with cross section $A$ and length $L$ in an insulating host material can be characterized by the conductivity $\sigma_{\text{net}} = G/L/A$. $\sigma_{\text{net}}$ scales near the percolation threshold with the power $p^{[69,139,140]}

![Figure 3.](image3.png)  
**Figure 3.** CNT bands as a function of strain. The strain-dependent valence and CBs ($\Phi_{v,p}(x, \epsilon)$) of the CNTs are depicted—as well as the strain-dependent bandgap $E_G$, the SBs $\Phi_{n,p}(\epsilon)$, and the electrostatic force $F = d\phi/dx$ at the contact. Three extreme cases are sketched—Fermi-level pinning ($\alpha=0.5$), VB pinning ($\alpha=0$), and CB pinning ($\alpha=1$).

![Figure 4.](image4.png)  
**Figure 4.** a) Sketch of the electrostatic potential in a CNT network. Straight lines symbolize CNTs, the color of the dots represents the value of electrostatic potential and the shaded areas are the contact sites. b) Sketch of the CNT intersection with the CNT–CNT distance $d$, the contact area $A$, the (schematic) energy landscape with the barrier height $\lambda$, and the electrostatic force $F$. Where $e$ is the elementary charge. Usually, $\lambda$ is a fit parameter and depends on the host material. Furthermore, the conductance can be converted into a tunneling probability by $p = G_{\text{jun}}/G_0$ with the conductance quantum $G_0 = 2e^2/h$.
\[ \sigma_{\text{net}} = \sigma_0 \cdot (p - p_c)^t \text{ with } p > p_c \text{ and } t \approx [1.6 \ldots 2] \]  

(9)

\( p \) is the (bond) percolation probability, \( p_c \) its critical value, and \( \sigma_0 \) the intrinsic material conductivity. Strain changes \( p \) such that \( p(e) = p_0 \) and \( \partial p / \partial e < 0 \), because the percolation probability \( p \) decreases with increasing strain. For example, Equation (7) results in \( \partial p / \partial e \approx -p_0 \beta_{G, \text{fin}} \exp(-B d_0 e) \).

The gauge factor for the CNT network is then

\[ \beta_{G, \text{net}} \approx -1 \cdot \frac{\partial p}{\partial e} (p_0 - p_1)^{-1} = -t \frac{\partial p}{\partial e} \sigma_{\text{net}}^{-1} \]  

(10)

which only depends on \( \partial p / \partial e \big|_{p=0} \) and beyond that, it is independent of the choice of the function \( p(e) \). This would imply that the gauge factor \( \beta_{G,\text{net}} \) monotonically decreases with increasing conductivity \( \sigma_{\text{net}} \), namely \( \beta_{G,\text{net}}(\sigma) \sim \sigma_{\text{net}}^{[0.5 \ldots 0.7]} \) —which is a universal observation in experiments (cf. Figure 5).

### 3.3. CNT Strain Sensor Performance from Experiments and Theory

The performance of the different CNT strain sensors is compared in Figure 5. It shows the gauge factor as a function of the conductance in case of swCNTs and as a function of the conductivity in case of CNT hybrid structures.

To compare different devices from several publications consistently, the differential gauge factor \( \beta_G \) is extracted in the limit of low strain. It becomes clear that—for any application—both the conductance and gauge factor should be acceptable. These quantities are inversely related,\(^{[54]} \) which is visible in Figure 5.

The comparison of different morphologies reveals that the gauge factor of contacted, single CNTs (cf. Figure 5, left) is usually higher than the gauge factor of CNT networks and thin films (cf. Figure 5, right). Even though the low strain sensitivity of CNT networks and thin films can be tuned with the parameter \( \frac{d\sigma}{de} \approx B d_0 = 4 \pi d_0 e V / \sqrt{2 \pi} \lambda / h \) (according to Equation (10)), the increase in the gauge factor is limited. A steady increase in \( d_0 \) by reducing the CNT density or manipulating \( \lambda \) due to an exchange of the host material automatically leads to a strong decrease in the conductivity—as the tunneling probability is inversely proportional to the quantities \( d_0 \) and \( \lambda \). This finally means that it is not easily possible to fabricate strain gauges from CNT networks and films with a comparable sensitivity to sensors based on the intrinsic piezoresistivity of single CNTs. In contrast, CNT networks and thin films are often much easier to produce and their strain range can reach \( 500\% \)\(^{[78,87]} \) whereas the strain range reported for N/MEMS-based approaches lies between 0.2\%\(^{[134]} \) and a few percent.\(^{[67]} \) Thus, the application scenarios for both sensing mechanisms are much different.

If the different swCNTs are compared with each other, two conductance regimes occur: semiconducting swCNTs possess a conductance of \( 10^{-6} \ldots 10^{-2} G_0 \), whereas semimetallic or small-gap swCNTs exhibit a conductance of \( 10^{-2} \ldots 10^0 G_0 \). Two data points, whose conductance is relatively large in the conductance regime, exceed a value of \( 560 \) many experiments report differential gauge factors in the order of \( 360 \), which is the maximum, intrinsic CNT gauge factor. With Schottky contacts, the total differential gauge factor can be enhanced up to \( 165\% \)\(^{[31]} \), yielding a value of about \( 560 \). Many experiments report differential gauge factors in the order of \( \beta_G = 500 \ldots 600 \)\(^{[31,34,62,64,66,67]} \) (cf. Figure 5, left).

Furthermore, the height of the SB determines the slope of the conductance versus the gauge factor (cf. Figure 6), which allows to estimate the SB of the given CNT-metal contact. As an example, the device of Helbling et al.\(^{[31]} \) would correspond to a SB of about \( 0.05 \ldots 0.10 \text{ eV} \), which is in line with the fact that they use semimetallic CNTs, owning a bandgap in the order of \( 100 \text{ meV} \).

During a quantitative comparison, it appears that the
conductance of the tunneling model overestimates the conductance of the experiment. This is not only due to defects in experiments, but also due to phonon scattering, which decreases the device conductance for typical CNT lengths in N/MEMS of about 1 μm, while hardly increasing the gauge factor.\textsuperscript{[54]}

The recent data of Böttger et al.\textsuperscript{[34]} show a similar trend: the error bars allow to determine the SB within 0.25...0.3 eV from Figure 5 and 6. The direct fit within the reference estimates $\Phi_{SB} = 0.27$ eV, which is in line with the device conductance as well as the behavior of $\beta_{GF}$ versus $G$, if one takes the a carrier transmission probability of about 10% into account.

Theory (cf. Figure 6, right) predicts a clear gauge factor maximum for a single kind of charge carrier, followed by a decrease in $\beta_{GF}$ upon further decreasing conductance $G$. This behavior cannot be reproduced by experiments, as there are two conductance branches: $p$-type and $n$-type. If, for example, $n$ conductance is decreased, $p$ conductance rises and starts to dominate the device behavior. This is the reason why the maximum of the experimental curves is sharp. In consequence, one can estimate the SB for both, $p$ and $n$ branch from Figure 5 (left).

Figure 5 (right) shows the gauge factor as a function of the conductivity for CNT networks and films, yarns, and composites from previous studies.\textsuperscript{[56,68,71,75,77,78,82,85,88–91,93]} Even though the values for $\beta_{GF}$ vary strongly, gauge factor and conductance are related quantities: the double-logarithmic plot of the gauge factor versus the conductance yields a power-law behavior for devices of the same formulation (i.e., types of CNTs and host material) but varying CNT content. The average scaling is given by $\beta_{GF} \sim \sigma_{net}^{0.21 \pm 0.04}$. The only exception is the data by Tong et al.,\textsuperscript{[91]} which scales with $\beta_{GF} \sim \sigma_{net}^{0.68}$. The reason for this can only be subject for speculations.

In contrast to most of the works, Nguyen et al.\textsuperscript{[90]} aim to produce CNT yarns, whose conductivity is strain independent and they arrive at a gauge factor as low as 0.15. Their recipe is to create CNT yarns with an extremely high conductivity, exceeding other CNT materials by about three orders of magnitude. The inverse scaling of the gauge factor with respect to the conductivity (Equation (10)) underlines how this recipe works.

Additional literature, which is not shown in Figure 5, is listed in Table 1 and 2. In most of these cases, conductivity could not be extracted.

Finally, we could show that the conductance and the gauge factor of strained swCNT devices are related—even though both quantities span orders of magnitude in current literature. This applies for strained CNT N/MEMS devices, where CNT transistors are integrated. Equation (4), (5), (7) describe the behavior of these devices—which is further justified by Böttger et al.\textsuperscript{[34]} Furthermore, percolation theory is the framework of choice to describe the gauge factor $\beta_{GF}$ as a function of $\sigma_{net}$ for CNT networks and thin films, obeying a power law of approximately the same exponent for many devices and simulations within current literature.

4. Conclusions

In total, this article classifies CNT morphologies used for CNT strain sensing, describes CNT testing methods for devices based on strained CNTs, and reviews the functionality of these devices in the light of theory. Percolation approaches describe the strain-dependent conductance of CNT networks and thin films, whereas thermionic emission and tunneling describes the strain-dependent conductivity of single CNTs.

The different CNT morphologies are either intrinsically or extrinsically strain dependent. For single and aligned CNTs or small CNT bundles, applied strain influences the intrinsic, electronic properties of the CNT material with respect to bandgap and SB so that the device conductance is significantly affected. The theoretical model of thermionic conductance and tunneling through the SB presented in this work is in line with the experimental observations. Especially the high gauge factors promote the strain dependence of both tunneling and thermionic conductance at the contact.

In a recent publication,\textsuperscript{[34]} it is envisioned that the tunneling effects—together with the low, intrinsic device capacitance—enable the fabrication of gateless CNT sensors. This would reduce the fabrication costs of those strain sensor devices enormously. Still, large amounts of characterization and testing are required to characterize for device reliability. Such reliability tests can be achieved by the SCA, as, e.g., promoted by Meszmer et al.\textsuperscript{[116]} Together with nanocharacterization, this gives insights into the nanoscopic failure mechanisms for CNT metal contacts.\textsuperscript{[109]}

Figure 6. Theoretical results of the strain-independent gauge factor $\beta_{GF}$ versus the conductance $G$ of a single CNT transistor, constituted by an armchair CNT with maximum strain sensitivity, as a function of the bandgap (left) and SB (right), when gate voltage is swept through. The black, dashed line denotes the maximum gauge factor. Left: The case of Ohmic contacts ($\Phi_{SB} = 0.5 \cdot E_G, \alpha = 1$ (see Figure 3), according to Wagner et al.\textsuperscript{[34]}, without phonon scattering. Right: The case of Schottky contacts at varying built-in field $F$, as described by Equation (4), (5), and (7).
For CNT networks and films or CNT yarns and fibers, strain acts on the CNT network: the change in the tunneling resistance between two adjacent CNTs changes and results in a change in the conductivity of the entire network. Literature data are in line with the theoretical result of the percolation model and prove (with one exception) that the critical exponent is indeed universal in CNT network structures. An upcoming trend is not just to use direct current to measure device sensitivity, but also alternating current (AC), as, e.g., promoted by Sanli et al.\[13\] P. Avouris, J. Chen, Mater. Today 2006, 9, 46.

Keywords

carbon nanotubes, micro- and nanoelectromechanical systems, reliabilities, sensors, strains

Received: July 15, 2019
Published online: October 2, 2019

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