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Nitrogen doping of metallic single-walled carbon nanotubes: n-type conduction and dipole scattering

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Abstract – The charge transport properties of individual, metallic nitrogen doped, single-walled carbon nanotubes are investigated. It is demonstrated that *n*-type conduction can be achieved by nitrogen doping. Evidence was obtained by appealing to electric-field effect measurements at ambient condition. *n*-type conduction is attributed to the presence of graphite-type nitrogen. The observed temperature dependencies of the zero-bias conductance indicate a disordered electron system with electric-dipole scattering, caused mainly by pyridine-type nitrogen atoms in the honeycomb lattice.

In the past, the electronic properties of multi- and single-walled carbon nanotubes (MWNTs and SWNTs) have been intensively investigated. The primary reason is that they represent an almost perfect model for fundamental research due to their unique one-dimensional electronic structure. For the same reason nanotubes are promising candidates for applications in molecular devices [1,2], provided their electronic properties, in particular the type of charge carriers, are controllable. Major efforts have been undertaken to this end including chemical modifications, [3] exposure to gaseous atmospheres [4–7] and immersion in electrolytes [8]. Another possibility for tailoring the nanotube's electronic system is their deliberate doping. In this case, doping refers to the substitution of a carbon atom with other elements such as nitrogen or boron and is expected to have significant impact on the nanotube's charge transport properties [9]. The successful nitrogen doping of MWNTs has already been achieved [10–13] and confirmed by thermopower measurements [12–14]. Only recently it was shown that it is possible to grow directly nitrogen-doped SWNTs, [15,16] reconfirmed by Raman and absorption spectroscopy [17]. Among these, the metallic SWNTs are of particular interest for the development of all-metal–based molecular nano-electronics. They represent excellent building blocks for devices with low power consumption in combination with large current densities. However, in standard SWNT devices *p*-type conduction is always observed. This results in severe limits on possible device architectures due to the absence of *n*-type conducting SWNTs.

Here we present the first investigation on individual metallic nitrogen-doped SWNTs, showing that intrinsic *n*-type conduction is achievable. Furthermore, in the low-energy limit, the charge carriers of nitrogen-doped SWNTs are found to display a temperature-dependent scattering mechanism, which is attributed to electric-dipole moment interactions. These two experimental observations are correlated to the different nitrogen bonding configurations in the carbon-host lattice. The nitrogen-doped SWNTs used had an average tube diameter of 1.2 nm and an average nitrogen content of 1 atom% [15]. In particular, the nitrogen is mainly bonded in two ways, pyridine- and graphite-like, c.f. fig. 1 [13,15,18]. Samples were prepared by standard electron-beam lithography [19]. As electrode material AuPd alloy on top of a SWNT was deposited. The distance between two neighboring electrodes was about

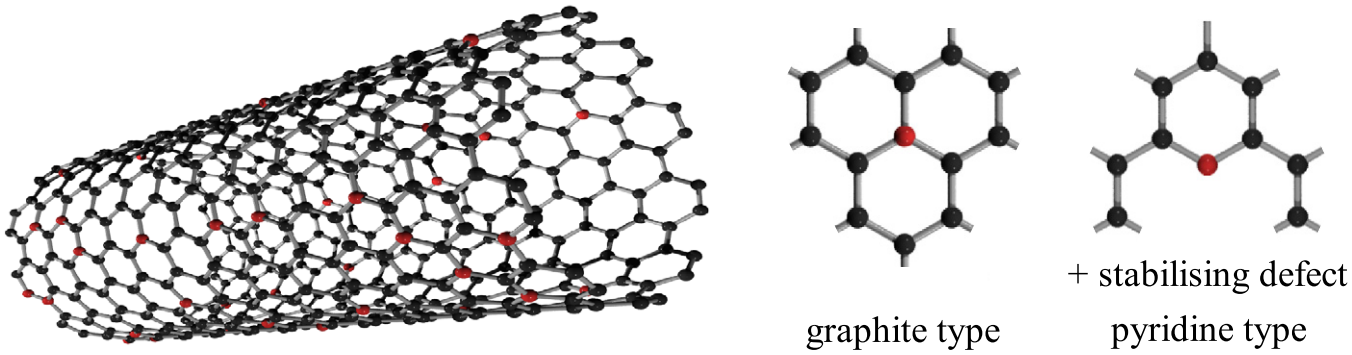

Fig. 1: Left: schematic view of a nitrogen-doped SWNT used in our measurements. Black and red balls correspond to carbon and nitrogen atoms, respectively. Right: the two main nitrogen bonds, graphite and pyridine type. Pyridine-type nitrogen is always accompanied with a stabilizing defect in the carbon lattice.

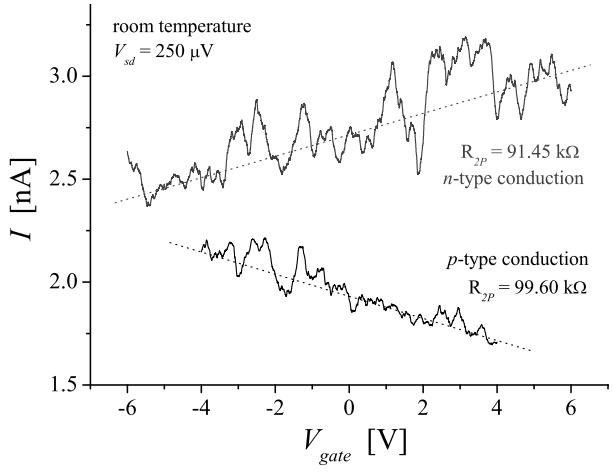

Fig. 2: *n*- and *p*-type conducting in nitrogen-doped nanotubes. Current response to the applied electric field (gate voltage) at room temperature. The source drain voltage was set to 250 μV. Curves for negative bias are equivalent (not shown). All curves exhibit fluctuations (fine structure), which are also observed in undoped carbon nanotubes.

200 nm. As substrate an n^+-doped Si-wafer with a 200 nm thick SiO_2 layer (thermally grown) was used serving as a back-gate.

In fig. 2 the transfer characteristic of two different nitrogen-doped SWNT samples, measured at room temperature (vacuum), are shown. As usual for metallic-like nanotubes, the observed current variation with the externally applied electric field is rather weak.

Both negative and positive slopes are observed, corresponding to *p*- and *n*-type conducting nitrogen-doped SWNTs, respectively. This is remarkable, because the nitrogen atoms are expected to act as electron donors. *p*-type conduction was observed in the majority of the samples investigated. This prevalence can be rationalized by a compensation of the number of additional, free electrons from nitrogen donor atoms by the number of additional acceptor states (environmental doping) [20,21]. However, this simplified picture is misleading: Nitrogen atoms are incorporated into the presently used SWNTs mainly in graphite- and pyridine-like ways [15]. For graphite-like nitrogen two of the valence electrons occupy the nitrogen's p_z-orbital [13]. Such nitrogen atoms can, in principal, be ionized and the liberated electrons can participate as excess electrons in the delocalized π-system. However, on the time average one of these two electrons is still to a certain degree localized [22]. In contrast, pyridine-like nitrogen cannot be ionized under ambient conditions, because two of its five valence electrons are in a non-bonding sp_2-orbital [13]. Therefore, this lone-pair will not participate in the conjugated bond system [23]. Thus, the two types of nitrogen bonding influence the thermodynamics and electrostatics of the SWNTs differently. At this point it is convenient to recall that the current investigation dealt exclusively with metallic tubes, *i.e.*, zero-gap semiconductors/semi-metals with a vanishing band overlap and a weak electric-field effect [24,25]. In undoped, electrically contacted metallic SWNTs the environmental doping, including work-function mismatches [20,21], modifies the Fermi energy position. From the initial charge neutrality point it shifts (varying with diameter, helicity, electrode material) into the π-band. In our samples (contact material AuPd) this shift is estimated to be ~ 0.6 eV [21,26,27]. The graphite-like nitrogen leads analogously to a Fermi-level shift towards the $\pi*$-band due to the excess electrons. According to a recent calculation with 2.8 atom% of nitrogen [23] this shift can be estimated to be smaller than 0.5 eV for our SWNTs (1 atom%). However, in our samples it is estimated that the amount of graphite-like and pyridine-like nitrogen are comparable [15]. Since the pyridine-like nitrogen does not contribute to the Fermi energy shift [23] 0.5 eV is even a stricter energy borderline. Consequently, a maximum difference in the Fermi level shifts of the order of 100 meV can be estimated in favor of the environmental doping. Consequently, only SWNTs with sufficiently high concentration of graphite-like nitrogen can be *n*-type conductors under standard device

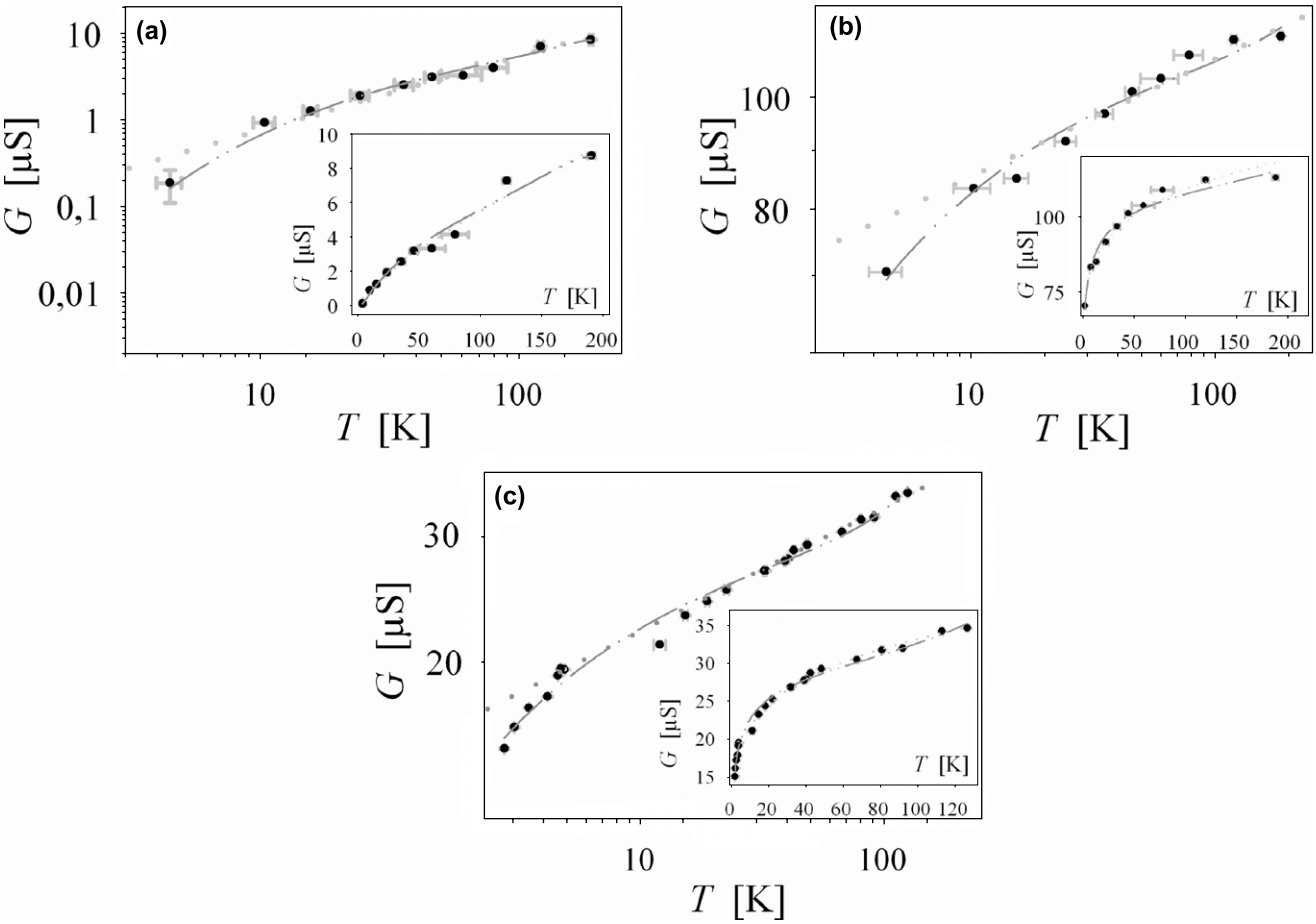

Fig. 3: Zero-bias conductance G *vs.* temperature T of three p-conducting nitrogen-doped SWNTs (double-logarithmic scale). Insets: $G(T)$ with linear axis. a) For sample A the data points above 5 K seem to coincide with a LL theory fit (dotted line). However, better agreement is obtained by the dash-dotted line which is based on a disordered state with $\tau(T) = \tau_0(1 - \lambda_\tau T)$ (eq. (1)). Coulomb-Blockade contributions have been determined by source-drain/gate-voltage sweeps. On that basis, data points have been corrected for these contributions. b) Sample B: the dotted line corresponds to a LL fit whereas the dash-dotted line is a fit based on eq. (1) showing a significantly better matching with the experimental data. c) $G(T)$ of sample C measured down to 2.7 K. The dash-dotted line is a fit based on eq. (1) and is in considerably higher agreement with the experimental data than a LL fit.

configuration and ambient conditions. Therefore, mainly p-type responses are expected, in agreement with our experimental findings.

In order to investigate the action of the nitrogen dopants as scattering centers, the low-energy charge transport of p-type conducting tubes is investigated. Since p-conducting tubes are investigated it is also implicitly proved that nitrogen dopants are present if deviations from p-conducting undoped nanotubes are observed [28]. The insets in fig. 3 show the zero-bias conductance, G, *vs.* temperature, T, for three samples. In all cases a clear suppression of G towards lower T is observed. The main graphs in fig. 3 show the same plot in double-logarithmic representation. The dotted lines are the theoretical fits for the tube's electron system, assumed to be in a Luttinger-liquid (LL) state: $G(T) \sim T^\gamma$, where γ is a function of the (dimensionless) interaction strength, g, between the charge carriers [28]. Noteworthy, g depends in principal also weakly on the Fermi level position (density of states) within the conduction bands close to the charge neutrality point. However, this dependence is neglected for the sake of simplicity. Sample A (fig. 3a) exhibits a rather weak electrical coupling to the electrodes (resistance about 108.1 kΩ) and at higher temperature appears to be in good agreement with the LL picture, with $\gamma \approx 0.77 \pm 0.05$. But this value of γ is in contradiction with previous theoretical and experimental values under comparable experimental conditions [28]. Also, the measurement point around 4.2 K deviates significantly from the LL theory. For sample B a clear deviation from the LL scenario (dotted line) is once more observed. Also, the low resistance of sample B at room temperature (about 8.2 kΩ) demonstrates that the nitrogen dopants cannot be primarily responsible for the variation of the two-point resistance experimentally

observed. Instead, the properties of the nanotube/metal interface is the main determining factor.

For sample C, $G(T)$ seems to follow a power law relation at higher temperature, but deviates significantly from this towards lower temperature. A detailed analysis, assuming a crossover from a LL to a disordered wire with neutral scatterers —implying a constant momentum relaxation time τ— reveals inconsistencies [29,30]. The linear part of the graph yields $\gamma \approx 0.2$ giving a value of g of about 0.4 ($g = N(\gamma\pi)^2/2$; N the number of conducting channels) [29]. For a fit describing the temperature dependence of the conductance of a disordered wire with constant relaxation time, a value of $g \approx 3.9$ was found by applying the expression $G(T) \sim exp(-\chi/T^{0.5})$ [29,30]. Here, the energy $\chi^2 = g/\pi N\tau$ (units $\hbar = k_B = 1$) accounts for the electrostatic charge carrier interactions. The discrepancy in the interaction strengths suggests that the theory used for the data analysis cannot account for our experimental results. Indeed, this conclusions is supported by the measurements at ambient condition. The pyridine-type nitrogen is likely to posses an electric-dipole moment analogous to pyridine, due to its lone-pair. However, because of the carbon host, the electric dipole's magnitude is expected to be significantly smaller than for a free pyridine molecule (2.215 D) [31]. The situation is more complex for graphite-like nitrogen. It is not bonded in a completely planar way, because of the carbon-lattice curvature. Furthermore, the excess electron is weakly localized, meaning that a dipole moment can exist. This dipole moment should be much smaller than the one induced by the pyridine-type dopants. Consequently, the nitrogen atoms, at least those of the pyridine type, cannot be regarded as neutral scatterers anymore but as electric-dipole scatterers. Other theoretically possible non-neutral (*e.g.*, magnetic) scattering mechanisms can be excluded for their relative weakness compared to the electric-dipole/electron-charge interaction [32,33][1]. Future theoretical studies should address these particular topics in more detail, but is beyond the scope of this work.

Therefore, because of the thermal fluctuation of the electric dipole moments, τ is temperature dependent [34]. These considerations require a small correction, which can be treated to a first approximation by $\tau(T) = \tau_0(1 - \lambda_\tau T)$ with $0 < \lambda_\tau \ll 1\,\mathrm{K}^{-1}$. On that basis, the temperature dependence of the observed zero-bias conductance $G(T)$ can be tentatively described by the phenomenological expression:

$$G(T) \sim (1 - \lambda_\tau T)^{-\gamma_\tau} \exp(-\chi_\tau/(T - \lambda_\tau T^2)^{0.5}). \qquad (1)$$

Dash-dotted lines in fig. 3 represent data fits according to eq. (1). In table I all results on the fitting parameters are summarized. The fit and the experimental data are in reasonable good agreement. Positive values for λ_τ of the order of magnitude of $10^{-3}\,\mathrm{K}^{-1}$ were found, in full agreement with the foregoing considerations. Some data-point fluctuations around the theoretical fits are observed suggesting possible higher-order scattering effects, which are not taken into account and should be subject of detailed future theoretical studies. However, the fundamental phenomenon that nitrogen atoms can act as electric-dipole scatterers in a carbon nanotube lattice remains valid. In particular, this data analysis on *p*-type conducting samples confirms that indeed nitrogen atoms are present in all SWNT samples investigated. It is worthwhile to mention at this point that according to recent calculations [35], interference effects involving the nitrogen dopants and the electrodes can principally lead to characteristic bias-dependent noise spectra and conductance fluctuations. Future experimental studies in this direction on any type of doped carbon nanotubes should consider these effects.

Table I: Charge transport parameters.

Sample	R_{2P} (kΩ)	γ_τ	χ_τ ($\mathrm{K}^{0.5}$)	λ_τ ($10^{-3}\,\mathrm{K}^{-1}$)
A	108.1 ± 0.2	0.77	8.97 ± 1.86	3.3 ± 0.5
B	8.5 ± 0.1	0.13	1.05 ± 0.04	2.9 ± 0.7
C	30.3 ± 0.1	0.20	1.16 ± 0.06	6.1 ± 0.4

In summary, we have performed electrical-transport measurements on metallic nitrogen-doped SWNTs under ambient conditions and in the energy limit of low temperature and zero bias. At room temperature, the results demonstrate, that *n*-type conduction can be achieved, depending on the graphite-type nitrogen concentration and the device design (environmental doping). Towards lower temperatures the zero-bias conductance is suppressed. The charge transport is better described by a disordered wire with nitrogen atoms acting as electric-dipole scatters than by a Luttinger-liquid state. Pyridine-type nitrogen is suggested to be the main contributor to this scattering process. A phenomenological expression for the zero-bias conductance was proposed, giving a good agreement with the experimental data. In turn, this proves that the tubes are doped with nitrogen, thus demonstrating that electrical transport also is a unique tool for probing low-concentration doping in nanotube systems. Thus, the synthesis of metallic SWNTs with more substituted graphite-like nitrogen than pyridine-like nitrogen or the substitution of higher-valence atoms than nitrogen is a reliable source for *n*-type metallic nanotube conductors, opening the field of all-metal molecular electronics.

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[1] Theoretically, a nitrogen dopant in a nanotube can exhibit a maximum magnetic moment of one Bohr magneton μ_B if (energetically unfavorable [32]) sp_2/sp_3-bond mixtures occur. In this case, the electric to magnetic dipole interaction strength ratio for a spin-1/2 charge carrier is determined by $\varepsilon_0^{-1} ep/\mu_0\mu_B^2 \sim 10^6\mathrm{nm}^{-1}$, assuming $p \approx 10^{-2}$ D as effective dipole moment (e electron charge, μ_0 and ε_0 magnetic and electric vacuum permittivity, respectively).

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