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Structure-dependent performance of single-walled carbon nanotube films in transparent and conductive applications

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Abstract

We investigate a complex relationship between structural parameters of single-walled carbon nanotubes (namely, mean length, diameter, and defectiveness) and optoelectrical properties (equivalent sheet resistance) of thin films composed of the nanotubes. We obtained a systematic dataset describing the influence of CO₂ concentration and growth temperature. On the basis of the experimental results, we prove the high Raman peak ratio (I_G/I_D), length, and diameter of the nanotubes to decrease the equivalent sheet resistance of the nanotube-based film. The approach employed highlights the change in the nanotube growth mechanism at the temperature coinciding with the phase transition between α -Fe and γ -Fe catalyst phases. We believe this work to be of high interest for researchers working not only in the field of transparent and conductive films based on nanocarbons, but also for those who reveals the fundamentals of the nanotube growth mechanism.

1. Introduction

Single-walled carbon nanotubes (SWCNTs) combine high conductivity with excellent optical and mechanical characteristics that make them a prospective component for novel electronic devices, *e.g.*, transparent conductive films [1,2] and field effect transistors [3]. Significant effort has been devoted to advance the field: active development of methods for SWCNT dispersion [4,5], separation [6], and purification [7]; utilization of post-treatment [8] and doping procedures [9], and even patterning [10] were shown to enhance the nanotube performance. Nevertheless, aerosol (floating-catalyst) chemical vapor deposition (CVD) method, which allows film fabrication by a dry transfer technique [11] avoiding laborious and expensive wet procedures, is within the spotlight. The aerosol CVD enables tuning of film conductivity during the synthesis that makes it preferable technology for thin-film applications of nanotubes [12]. However, despite the abundance of realized approaches the current state-of-the-art SWCNT-based transparent conductive films (TCFs) still have not met the industrial requirements, being inferior to metal-oxide counterparts (*e.g.* indium-tin oxide) [13].

As a rule, numerous studies related to the fabrication of highly transparent and conducting SWCNT films using the aerosol CVD technique consider the influence of the growth parameters on the optoelectronic performance: effect of different carbon sources [14–16], catalyst composition [17,18], synthesis temperature [19], reactor design [20], *etc.* Though the most of publications in the field refer optoelectronic performance to the structural aspects of the SWCNTs (diameter distribution [21], bundle size [22,23], electronic structure [24], *etc.*), the complex relation between reaction parameters and SWCNT structure results in controversial or incomparable trends [25] and conclusions [26,27]. Such a lack of a proven and direct connection inhibits the targeted optimization of SWCNT-based TCF performance and, thereby, the implementation of SWCNT-based devices.

Here, we disentangle the complex relations between the structural parameters of SWCNTs (namely, length, diameter, and defectiveness) and performance of the nanotube-based TCFs. We

assess the systematic dataset of SWCNT samples with a comprehensive set of methods providing a deep characterization of the SWCNT structure. We believe this work is to guide the path towards advanced carbon nanotube performance for optoelectronic applications.

2. Experimental

2.1 Sample preparation

We synthesized SWCNTs using an aerosol (floating-catalyst) CVD reactor operating at atmospheric pressure described in details elsewhere [28]. Briefly, the reactor consisted of a quartz tube placed in the three-zone furnace (800–1050°C) with an isothermal zone of 70 cm. Ferrocene vapor (0.9 Pa at 24°C [29]) introduced directly into the reactor hot zone with 1000 sccm CO flow passed through a cartridge with ferrocene/silica mixture. Additionally, the flow of a CO/CO₂ mixture was introduced from the main inlet. A volumetric fraction of CO₂ was tuned up to 2.2 vol. %, while the total flow rate through the reactor was fixed at 5000 sccm. Carbon nanotubes grown in gas phase were collected at the outlet of the reactor using nitrocellulose membrane filter (MF-Millipore, 0.45 µm pore size). Collected films were dry-transferred [11] on a glass slide for subsequent characterization.

2.2 Sample characterization

We utilized absorption spectroscopy, measured in the wavelength range from 300 to 2600 nm, (Perkin Elmer UV-vis-NIR spectrophotometer Lambda 1050) to estimate the yield and mean diameter of produced SWCNTs. Mean diameter was determined from the position of S₁₁ transition peak position according to reference data provided [30], while yield was associated with absorbance at the wavelength of 550 nm. The yield was calculated as a rate of the collection of 90% transmittance (T) film:

$$yield[min^{-1}] = \frac{\log_{0.9}(T)}{t}$$

Here, we fixed the flow rate through the nitrocellulose Millipore HAWP filters (11 mm diameter, 0.45 µm mean pore size) used to be equal to 3800 sccm, while collection time (t) was varied.

The quality of carbon nanotubes was investigated by Raman spectroscopy (Thermoscientific DXRxi Raman Imaging microscope) with an excitation wavelength of 532 nm. Spectra were collected at 0.1 mW (the lowest available) laser power with 0.16 s exposure time and >100 frames averaging; laser beam spot size was estimated to be several micrometers. Measurements were repeated at least in

three positions of a sample and nonuniformity of Raman response along the sample was found to be negligible (signal-to-noise ratio value was above 500).

To measure the sheet resistance of the films we used a four-probe station Jandel RM3000. The measurements for each film were repeated at least three times (at various angles between film and probes) and obtained values were averaged. The current was varied from 0.01 to 1 mA depending on a sample conductivity. The SWCNT length distribution was investigated by scanning electron microscopy (SEM, JEOL JSM-7001F) on a Si/SiO₂ substrate. The individual SWCNTs were deposited directly from the gas phase on substrate placed on membrane filter.

A differential mobility analyzer (DMA) equipped with a condensation particle counter (Scanning Mobility Particle Sizer Spectrometer 3938, TSI, USA) was employed to study the SWCNT aerosol size distribution. The device allowed us to measure an effective diameter, which corresponds to the size of a spherical particle with a single charge possessing the same electrical mobility, in the range from 1 to 1000 nm. The technique allows one to distinguish the conditions of inactive catalyst particles (usually with the effective mobility diameter below 20 nm) from the conditions of nanotube synthesis (40-100 nm) [31] .

3. Results and discussion

We employ the ferrocene-based aerosol CVD technique [11] for SWCNT growth by means of the Boudouard reaction. Changing the growth conditions, namely the temperature (in the range of 800-1050 °C [32]) and CO₂ concentration (0-2.2 vol. %; moderating the catalyst performance [28,33]), we have gathered the dataset of 70 points. The vast collection of employed methods provided the complex insight over the key characteristics of both individual nanotubes and SWCNT films: mean diameter, yield (absorbance of the film collected with a specific time and catalyst supply), quality (the ratio of G and D modes of a Raman spectrum; I_G/I_D), and sheet resistance.

The dataset describes the correlation trends between nanotube structural parameters (I_G/I_D , diameter) and SWCNT film optoelectronic performance, providing a comprehensive insight into the correlations hidden by complex association of the parameters. Figure 1a illustrates the relation between the I_G/I_D ratio and equivalent sheet resistance (sheet resistance of a film with 90%

transmittance at 550 nm) [15]. We observe an intuitive monotonic change validating a common phenomenological rule “lower defectiveness of carbon nanotubes results in higher conductivity of thin films” [34] with the lowest value of $430 \Omega/\square$ corresponding to I_G/I_D ratio equal to 330.

Figure 1. The correlation between equivalent sheet resistance of SWCNT films produced at temperatures from 800 to 1050 °C (highlighted with color) as a function of (a) I_G/I_D , (b) mean diameter and (c),(d) yield.

A recent finding that “thicker SWCNTs lead towards lower resistance” [21] mostly satisfies the data (Figure 1b). However, an increase in the equivalent sheet resistance is observed for several points corresponding to the diameter of 2 nm (typically the highest diameter for CO-based aerosol CVD [28]). This inconsistency could be attributed to CO_2 excess resulting in a high fraction of iron impurities (discussed further), and as follows, negatively affecting the performance [35]. However, the dataset ought to be enlarged to prove the observed trend. It should be noted that we found the SWCNT diameter and I_G/I_D to be linear independent parameters (Figure S1). Thus, we confirmed

SWCNTs of higher quality (according to I_G/I_D) and larger diameter (corresponding to lower contact resistance between tubes [21]) to result in lower equivalent sheet resistance that in a good agreement with the previous findings for the CO-based synthesis [11].

An interesting feature can be observed when the dataset is plotted in yield- R_{90} coordinates (Figure 1 c,d): at $T < 925$ °C the R_{90} values are downward function of yield, while above 925 °C there is no correlation between R_{90} and the yield. This peculiarity indicating a change in a growth regime can be attributed to the complex nature of the yield: it depends not only on the length but also on the catalyst activation degree. Indeed, we revealed the yield to be a monotonic function of SWCNT length for the growth $T < 925$ °C, that was not the case of higher temperatures: there was no correlation between the yield and the nanotube length (Figure S2 a,b). In addition for the whole temperature range the relationship between SWCNT length and R_{90} is similar (Figure S2 c,d) indicating the yield to be strongly dependent on the activation degree of the catalyst. To study the transition in SWCNT growth mechanism we employed the Arrhenius plot (Figure 2a). While the effect of CO_2 is also a complex and temperature-dependent phenomenon, we have used carbon dioxide-free growth to conduct an unambiguous analysis. Interestingly, we discovered the bend of the kinetic curve at *c.a.* 900 °C, which splits into two parts with different observed activation energies (E_a): $E_a^{highT} = 154 \pm 19$ kJ/mole for high and $E_a^{lowT} = 182 \pm 14$ kJ/mole for low temperature ranges.

The apparent transition temperature of 900 °C is close to the phase transition point between α -Fe and γ -Fe (Figure 2b). Although the phase transition is observed at 912 °C for bulk iron, the phase diagram might be shifted for nanometer-size particles [37]. Unfortunately, the architecture of the aerosol CVD method restricts most of *in situ* methods closing the window for a direct proof by, *e.g.*, *in situ* XRD [38] or *in situ* TEM [39]. Nevertheless, the high-temperature activation energy of 154 kJ/mole is consistent with previously reported value of 137 kJ/mole, associated to carbon diffusion in γ -Fe (stable at $T > 912$ °C) [40]. Moreover, the value of 182 kJ/mole (low-temperature regime) fairly

well fits with the results reported on carbon diffusion in cementite [41] (Fe_3C), usually related to α -Fe (stable at $T < 912^\circ\text{C}$) [42,43]. It should be noted that the activation energy for CO dissociation on a surface of iron nanoparticle was also found to be of 189 kJ/mole (1.96 eV) [44] for α -Fe and 106–205 kJ/mole for nanometer-size γ -Fe [45]. Here, we consider only kinetics of the reaction because estimated conversion of CO into CO_2 (section S4) in our case is infinitesimal compared to calculated equilibrium pressure of CO_2 (Table S2) that indicates the reaction is not reaching equilibrium.

Figure 2. (a) Temperature kinetics of SWCNT yield plotted in Arrhenius coordinates. (b) Bulk iron-carbon phase diagram adapted from [36]. Two temperature regions, corresponding to linear relations with different slopes, are attributed to the change of the reaction-determining process, schematically depicted in (c). (d) Calculated melting temperature for α - and γ -Fe (blue and red curves) and temperature of α - γ phase transition of iron (purple curve).

To check whether phase transition is possible for Fe nanoparticles, we estimate the influence of the size-effect on phase transition temperatures (Figure 2d; more in section S4). The recent findings of CO-based SWCNT growth postulate that active Fe nanoparticles are several times larger than corresponding nanotube diameter and are roughly estimated to be 2-6 nm in our case [46]. Thus, according to calculations we can conclude that catalyst nanoparticles still could be crystalline under the conditions studied or at least have a solid core with melted surface.

The role of carbon dioxide in the Boudouard reaction-based SWCNT growth is usually considered to be similar to the water performance within the super growth process [47,48]: it etches excessive carbon-based intermediates on the catalyst surface, while inhibiting the SWCNT growth under high concentrations. We found that the phase transition of catalyst does not show any substantial impact on the role of carbon dioxide (Figure 3a). It should be noted that due to extremely low conversion of CO in aerosol CVD, the system is supposed not to reach equilibrium during the growth (section S3).

Figure 3. (a) CO₂ effect on SWCNT yield for temperature 825 °C (blue) and 1000 °C (red); (b) temperature-dependence of total concentration of the SWCNT aerosol particles measured using the particle size spectrometer; grey line represents transition temperature region discussed previously.

Surprisingly, the iron phase transition affects only the yield (Figure 1), while the diameter distribution (Figure S3a) and I_G/I_D (Figure S4a) show smooth lines without any features at $T \approx 900$ °C.

Since the yield is a complex function of the catalyst lifetime (corresponding to SWCNT length), catalyst activation degree (the ratio of active Fe particles), and amount of amorphous carbon (negligible for CO-based synthesis; Figure S4e), the change in “ R_{90} – Yield” relation can be accounted to a shift in yield-determining process. As it was discussed, below 925 °C the yield is implied to be mostly determined by the length of SWCNTs, while above the catalyst activation degree plays the crucial role. While length significantly impacts the equivalent sheet resistance of the film [22], the catalyst activation degree might only affect it via the minor contribution of Fe nanoparticles in the transmittance [8] that explains different behavior of “ R_{90} – Yield” relations. We examined whether the change in catalyst activation degree takes place with a scanning mobility particle size spectrometer (Figure 3b; number-size distributions are presented in Figure S7) revealing a significant gain in the concentration of aerosol particles (nanotubes) at $T > 900^\circ\text{C}$ while the concentration of the catalyst was kept constant.

4. Conclusion

Summarizing, we extensively investigated the correlation between nanotube structural parameters and optoelectrical properties of SWCNT films synthesized CO-based aerosol CVD with Fe-based catalyst. We link the performance of SWCNT-based transparent conductive films (equivalent sheet resistance) with the carbon nanotubes of the lowest defectiveness (ratio of G and D modes of a Raman spectrum) and high diameter reaching the equivalent sheet resistance of the pristine films of $430\ \Omega/\square$. The SWCNT growth splits into two temperature regions (by the means of yield): length-dependent ($T < 925^\circ\text{C}$) and activation degree controlled ($T > 925^\circ\text{C}$). The latter corresponds to no effect of the yield on the SWCNT thin film performance, while the nanotube length (and, as follows, yield in low temperature region) is shown to decrease the equivalent sheet resistance. The change in the yield-determining factor (900-925 °C) can be accounted for the phase transition of Fe

catalyst ($\approx 912^\circ\text{C}$). The obtained results could contribute to the targeted tuning of SWCNT thin film properties for the advanced optoelectronic devices.

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