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Highly individual SWCNTs for high performance thin film electronics

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ABSTRACT

We report a continuous floating catalyst chemical vapor deposition synthesis of highly individual single-walled carbon nanotubes (SWCNT) for high performance transparent conducting films (TCF). Active feedback dilution of ferrocene-based catalyst vapor leads to an almost complete elimination of SWCNT bundling and a substantial increase in SWCNT lengths via the suppression of bundling-induced growth termination. The fabricated uniform TCFs exhibit sheet resistances of 89 Ω/sq. at 90% transmittance. This was further improved by micro-patterning, resulting in a sheet resistance of 69 Ω/sq. at 97% transmittance – the highest reported for any carbon nanotube TCF – and highly competitive with commercial indium-tin-oxide-TCFs. Furthermore, we demonstrate that thin film transistors fabricated from these highly individual SWCNTs reach charge carrier mobilities up to 100 $cm^2 V^{-1}s^{-1}$ and ON/OFF-ratios up to 10^6.

1. Introduction

Single-walled carbon nanotubes (SWCNT) have exceptional application potential in thin film electronics due to their unique electrical and optical properties, which can be exploited in variety of applications, including transparent conductive films (TCFs) [1–7] and thin film transistors (TFTs) [8–13]. SWCNT networks can be fabricated using a variety of techniques, such as spray coating and press transfer, and they exhibit high flexibility, high maximum transmittance and low sheet resistance [6,7,14]. SWCNT networks have been also used to fabricate TFTs via transfer processing of dry fabricated SWCNT networks [12,13] or by inkjet and gravure printing [15,16], resulting in high charge carrier mobilities and ON/OFF current ratios. Combined, these enable the potentially high throughput fabrication of SWCNT based flexible integrated circuits. Almost all SWCNT synthesis processes, such as arc discharge, laser ablation and HiPCO, produce a mixture of SWCNTs, bundles, by-products and impurities, necessitating extensive purification and dispersion treatments before their use in electronic applications [17]. These are detrimental for performance, as high power ultrasonication induces defects and shortens SWCNTs, while surfactants used for aqueous dispersion can be difficult to remove, leading to high contact resistances and limited device performance [2,18–20]. Dispersion of SWCNT bundles is also essential prior to liquid phase helicity separation techniques, such as density gradient ultracentrifugation [21] or gel chromatography [22], which can be used to separate semiconductive and metallic SWCNTs. Elimination of these processing steps is necessary for the industrial production of SWCNT based components. For ultimate efficiency, synthesis and deposition processes must be developed to enable the direct fabrication of individualized SWCNTs with narrow chirality distributions.

Floating catalyst chemical vapor deposition (FC-CVD) is a promising SWCNT synthesis technique with reduced dependency on liquid processing [23]. It enables the direct, single-step fabrication of clean and ready-to-use SWCNT networks. The process has been used for the fabrication of high performance SWCNT TCFs [6,7] and TFTs [12,13]. Previous studies have shown that the SWCNT and bundle morphologies have a major impact on the performance of SWCNT networks [6,12,24]. First, increasing bundle length correlates with decreasing sheet resistance at a constant optical transparency, as longer bundles reduce the amount of high resistance inter-bundle contacts in the network [6]. Second, the importance of long, extended y-type contacts and small diameter

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bundles has been demonstrated in the context of low-density SWCNT networks for TFTs [12] and by spatially resolved conductive-AFM characterization of inter-tube contacts [24]. Third, individual SWCNTs are also indispensable for the efficient electrostatic gate-channel coupling in SWCNT thin film transistors [12], with reduced SWCNT bundling also helping to decrease the probability of metallic short circuited channels in SWCNT TFTs [25]. Finally, gas phase bundling is expected to lead to SWCNT growth termination, and thus for optimal SWCNT TCF performance requiring long SWCNTs, bundling should be reduced or completely eliminated.

2. Experimental

Our SWCNT synthesis process is based on the low vapor pressure organometallic compound, ferrocene, which is sublimated in a flow of carbon monoxide (CO). The ferrocene-containing gas is injected through a water-cooled injector probe, maintained at a constant temperature of 24 °C, into a high temperature synthesis reactor whose maximum temperature is 880 °C based on previous process optimization [6]. The ferrocene is thermally decomposed to iron vapor in the steep temperature gradient immediately after exiting the water-cooled injector. The iron vapor subsequently nucleates into iron nanoparticles, which catalyze the SWCNT growth by the Boudouard reaction in the laminar flow inside the synthesis reactor. The reactor chamber consists of an inert-walled quartz tube of 560 mm in length and 22 mm in diameter. The grown SWCNTs can be collected at the reactor outlet by membrane filtration as randomly oriented SWCNT networks, which have been previously shown [6] to primarily consist of small diameter SWCNT bundles around 10 nm in diameter.

The probability for aerosol particles to collide, leading to bundling, has a quadratic dependence on the particle concentration [26],

$$\frac{dN}{dt} = -K_0 N^2, \quad (1)$$

where N is the aerosol number concentration and K_0 is the size and temperature dependent coagulation coefficient. This suggests that collisions between SWCNTs can be suppressed by reducing the number concentration of the SWCNT aerosol. The catalyst particle concentration and subsequent SWCNT concentration depend on the amount of ferrocene introduced into the reactor. Here, the ferrocene cartridge was placed in a water-cooled heat bath maintained at 24 °C to maintain a stable catalyst precursor vapor pressure. To further improve concentration control, we developed an on-line monitoring and feedback system, schematically depicted in Fig. 1. The system is based on microprocessor-controlled mass flow controllers (GFCS series, Aalborg Instruments, USA) for the controllable mixing of ferrocene-containing CO with pure CO for catalyst concentration adjustment, together with fast aerosol monitoring at the reactor outlet using a differential mobility analyzer and a condensation particle counter (5414 CPC with medium length Vienna type DMA, Grimm Aerosol Technik GmbH). The system improves the reproducibility and stability of the SWCNT synthesis process, enabling rapid feedback of the synthesis process. For concentration-controlled FC-CVD synthesis, a minor fraction of the CO flow was passed through the ferrocene saturator (volumetric flow of 50–100 ccm) and mixed with pure CO downstream of the saturator cartridge (200–250 ccm). To maintain constant particle concentration, the mixing ratio of ferrocene-saturated and pure CO flows was varied while maintaining the total main flow at 300 ccm. Fig. 1b shows the acquired SWCNT number size distributions at different ferrocene concentrations, measured by the DMA system probing the floating structure concentration vs. electrical mobility diameter D_p. The feedback system significantly improved the temporal stability of the FC-CVD process, leading to less than 10% standard deviation in concentration over 40 h (Fig. 1c). Interestingly, high resolution TEM (HR-TEM) imaging in a JEOL JEM-2200FS operated at 80 kV (Fig. 1 d–f) suggests that the increasing ferrocene concentration leads to increasing bundling, clearly observable in samples directly deposited on TEM grids at the reactor outlet.

For this work, the FC-CVD process was operated at three specific conditions: 1) Low concentration, where approximately 50 ccm of CO was passed through the ferrocene cartridge, leading to a total particle concentration of 0.25×10^6 #/cm^3; 2) Medium concentration, 75 ccm flow through the cartridge, particle concentration 1.2×10^6 #/cm^3; and 3) high concentration, 100 ccm flow through the cartridge, particle concentration 2×10^6 #/cm^3. The total particle concentrations were deduced by integrating the area under normalized number size distributions shown in Fig. 1b. Randomly oriented SWCNT networks from each condition were deposited on membrane filters and subsequently transferred by room-temperature press transfer [6] onto high transparency quartz slides (HSQ300, Heraeus GmbH) for optical spectroscopy and electrical characterization, or to flexible polyethylene naphthalate substrates (PEN 65FA, 100 μm, Teijin-DuPont, Japan) for flexible TCF fabrication. The absorbance measurements were carried out using PerkinElmer Lambda 950 spectrometer (PerkinElmer, Inc., USA) and sheet resistances were acquired using a Jandel Ltd. 4-point probe at 60 g needle loading and 250 μm tip radius for the uniform SWCNT TCFs.

For the line grid patterned SWCNT TCFs the sheet resistance was estimated by depositing silver paint (Leitsilber 200N) contacts at the edges of a square are covered by the grid pattern of 10 mm × 10 mm and by performing 2-terminal resistance measurement by using Agilent 34410A multimeter at moderate measurement current of 10 mA, to avoid excessive Ohmic heating. The current was supplied in direction parallel to the horizontal lines in the Fig. 4c, and the measured grid area was limited by mechanical cutting along the measurement area edges. Electrical contacts to the sample were formed by using Suss Microtech PA150 probe station equipped with tungsten carbide needles on precisely controllable micromanipulator for stable and low resistance mechanical contact to the silver paint contact areas. The optical transparency was measured by limiting the beam size to 10 mm × 5 mm area which was completely covered by the grid pattern, thus effectively measuring the average transparency over the grid pattern.

Our results show that lower ferrocene concentrations lead to substantially improved TCF performance. Pristine, as-collected SWCNT TCFs from the high and medium concentration conditions exhibited sheet resistances of 5 and 1.3 kΩ/sq. at 90% transmittance, whereas the low concentration leads to SWCNT TCFs of 950 Ω/sq. (Fig. 2a). Chemical doping is a well-established method to further improve the sheet resistance of SWCNT networks by charge-transfer induced Fermi level shifting and subsequent increase in charge carrier density [4,27]. To further improve TCF performance and to enable direct comparison with our previous work, we used a rapid post-deposition treatment, consisting of densification and wetting SWCNT network by concentrated nitric acid (65% HNO_3, J.T. Baker, Netherlands) for 60 s [6]. The acid treatment reduced the sheet resistances of the high, medium and low concentration films to 440, 120 and 89 Ω/sq. at 90% transmittance, respectively. Interestingly, SWCNT networks collected from the low concentration conditions exhibited highly resolved E_{11} and E_{22} peaks in optical absorption spectroscopy. These peaks are related to optical transitions between the first and second van Hove singularities of semi-