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Synthesis and cryogenic spectroscopy of narrow-diameter single-wall carbon nanotubes

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ABSTRACT

We report chemical vapor deposition and cryogenic photoluminescence studies of narrow-diameter single-wall carbon nanotubes. Our systematic study of synthesis parameters identifies means to control the average length, diameter, and areal density of carbon nanotubes grown on silica substrates. Using synthesis conditions that favor the growth of carbon nanotubes with sub-nanometer diameters, we fabricate samples with spatially isolated suspended nanotubes ideally suited for optical studies. Photoluminescence spectroscopy of individual nanotubes reveals two classes: spectrally broad and narrow single-peak emission at the temperature of liquid helium. The latter class with spectral line widths down to the resolution limit of our spectrometer of 40 μeV indicates that exciton coherence in carbon nanotubes can be substantially improved by controlling the growth conditions and utilized in sources of indistinguishable single photons.

1. Introduction

Optical transitions of electron-hole pairs (excitons) [1,2] in semiconducting carbon nanotubes (CNTs) enable a wealth of potential optoelectronic applications [3] ranging from solar light harvesting devices [4] to single photon emitters [5] up to room temperature [6] for quantum cryptography and communication. In contrast to numerous studies of the optoelectronic properties of CNTs carried out on micelle-encapsulated nanotubes [7], reports on the photophysics of as-grown narrow-diameter CNTs with exciton photoluminescence (PL) at the lower wavelength edge of the CNT emission [8] have been sparse despite the technologically relevant window of silicon-based detectors with superior signal-to-noise performance, and the fundamental relevance of electron-hole Coulomb correlations that scale inversely with the nanotube diameter [9]. This is mainly owed to the facts that most synthesis methods for single-wall CNTs are neither chirality-selective nor do they yield abundant CNTs with sub-nanometer diameters and corresponding PL emission wavelengths below 1000 nm [8], and that non-suspended as-grown tubes in contact with the substrate suffer from significant PL suppression [10].

The limited control of diameter-specific CNT growth is primarily a consequence of the complex interplay of the numerous synthesis parameters such as catalyst composition, size and pretreatment, carbon precursor, additives, temperature, or substrate support in catalytic chemical vapor deposition (CVD). Although this complexity has impeded a thorough microscopic understanding of the details involved in the CNT synthesis, remarkable progress has been achieved in the structural control of CNTs by means of catalyst design [11,12]. Variation of catalytic metals explored in other studies has indicated that single-wall CNTs with sub-nanometer diameters can be preferentially obtained under appropriate growth conditions [8,13–18]. Combined with the synthesis on structured substrates in the form of pillars [19] or trenches [10], samples with isolated as-grown narrow-diameter CNTs can thus be realized for fundamental studies of intrinsic optoelectronic properties [20] not compromised by side-wall wrapping molecular surfactants.

In the following, we present the results of our studies that aimed at realizing as-grown narrow-diameter CNTs isolated from the substrate for optical spectroscopy. We demonstrate how a significant fraction of CNTs with sub-nanometer diameters and PL emission wavelengths below 1000 nm can be obtained with optimized catalytic CVD synthesis. We investigated the impact of various CVD

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parameters on the nanotube lengths, diameters, and areal density, and employed an optimized synthesis method for the growth of individual narrow-diameter CNTs suspended on perforated membranes. PL spectroscopy of individual suspended nanotubes revealed two regimes of CNTs with single-peak emission at the temperature of liquid helium (4.2 K): in accord with previous studies we found CNTs with PL line widths in the range of a few millielectronvolts [21,22] and substantially below 1 meV [22,23] down to the resolution limit of our spectrometer.

2. Experimental

Our CVD process is based on methane in the presence of a bimetallic iron-ruthenium (FeRu) catalyst that has been reported to promote the growth of nanotubes with diameters of ~1 nm [15]. By choosing methane as the carbon feedstock for nanotube synthesis, amorphous carbon contamination is reduced due to its kinetic stability [24] and molecular decomposition is primarily assisted by the catalyst particles. Moreover, we used additional hydrogen gas which has been shown to promote the growth of clean CNT samples [25]. The FeRu catalyst was prepared from three stock solutions consisting of iron(III) nitrate nonahydrate ($Fe(NO_3)_3 \cdot 9H_2O$), ruthenium(III) chloride hydrate ($RuCl_3 \cdot xH_2O$), and alumina nanoparticles each dissolved in isopropyl alcohol. Concentrations of the stock solutions were chosen to be 4.65 g/l, 1.40 g/l, and 1.50 g/l, respectively. The solutions were stirred over night before small amounts were mixed together and diluted with isopropyl alcohol to obtain a catalyst solution with ingredient concentrations of 116.1 mg/l iron(III) nitrate nonahydrate, 35.0 mg/l ruthenium(III) chloride hydrate, and 37.5 mg/l alumina particles.

To control the areal density of the CNTs on silica, the solution was diluted further with isopropyl alcohol and bath-sonicated for 2 hours before its spin coating on the Si/SiO_2 substrate resulted in nanometer-sized catalytic particles on the surface. In selected cases we treated the catalyst particles with an oxygen plasma that was provided by a standard plasma etcher (LabAsh 100) operated at 2 torr and 55 W for 180 s prior to the CVD process.

For nanotube synthesis the samples were transferred into the middle of our CVD system consisting of a tubular furnace (Nabertherm R40/500/12-B170) and a quartz tube measuring 130 cm in length and 32 mm in inner diameter (wall thickness: 2 mm). The furnace was heated to a growth temperature in the range of 700–900 °C at a flow rate of 1.5 standard liters per minute (slm) of inert argon with 5% hydrogen. After reaching the growth temperature the CVD tube was flushed with hydrogen at 1.0 slm for 5 min to reduce the catalyst particles. Subsequently, methane and hydrogen with a fixed CH_4/H_2 flow rate ratio of 1.33 were passed through the reaction chamber for carbon nanotube synthesis. Under these conditions the growth was maintained for 10 min. Afterwards the supply of CH_4 was stopped and the samples were gradually cooled in a hydrogen flow at 0.5 slm. At a temperature of ~500 °C hydrogen was replaced by argon with 5% hydrogen. Finally, the samples were unloaded at a furnace temperature of ~300 °C.

To obtain suspended CNTs we employed our CVD method on perforated silicon nitride substrates (DuraSiN Mesh for TEM, DTM-25233) with holes and craters 2 μm in diameter. To maintain the surface growth conditions of silica, the silicon nitride substrates were covered with a 100 nm thick layer of SiO_2 by plasma enhanced CVD (Oxford Instruments Plasmalab 80 Plus) prior to drop casting the catalyst solution onto the sample surface and subsequent blow-drying with nitrogen.

Carbon nanotube length and areal density data from CNTs on Si/SiO_2 was acquired by imaging the fabricated samples with a scanning electron microscope (Raith e_Line) at an electron acceleration voltage of 0.7 keV. The CNT diameters were determined by height profiling with tapping mode atomic force microscopy (AFM) (Digital Instruments Dimension 3100) under ambient conditions.

Cryogenic PL studies of individual CVD-grown CNTs were performed in a home-built confocal microscope in backscattering configuration at the temperature of liquid helium (4.2 K). The samples were positioned with respect to the excitation and detection spots of the microscope objective (Thorlabs C330TME-B) by a combination of nanometer-precise piezo steppers (attocube systems ANPxyz101) and scanners (attocube systems ANSxy100). Optical excitation was provided by a continuous wave titanium-sapphire laser (Coherent Mira900) at a fixed wavelength in the range of 730–850 nm. The PL of individual CNTs was filtered from laser background with a long-pass filter (Omega Optical 860AELP, cut-on at 860 nm), dispersed with a grating monochromator (Princeton Instruments Acton SP-2558) and recorded with a liquid nitrogen cooled low-noise silicon CCD (Princeton Instruments Spec-10:100BR/LN) with a lower detection limit of ~1.18 eV. The upper limit of the detection window was set by the long-pass filter to ~1.44 eV. By raster-scanning the sample with respect to the focal spot of the excitation laser and recording a PL spectrum at each displacement position we acquired spatio-spectral maps of individual sample regions with a spatial resolution of 1 μm and a spectrometer-limited spectral resolution of ~40 μeV.

3. Results

3.1. Influence of the synthesis parameters on carbon nanotube growth

Fig. 1a shows a representative scanning electron microscopy (SEM) image of CNTs grown on a Si/SiO_2 substrate. The growth temperature and the methane/hydrogen flow rate were 850 °C and 1.0 slm/0.75 slm, respectively. The median of 1.2 μm of the length distribution was extracted from a log-normal distributional fit to the data (Fig. 1b). We also studied the influence of the CVD temperature on the median length but found no significant dependence. However, similar to the results of Yang et al. [26], the nanotube lengths increased reproducibly by treating the deposited alumina-FeRu catalyst particles in an oxygen plasma prior to the CVD process. The increase was attributed to an immobilization of the catalyst particles on the support, thereby effectively suppressing particle coarsening and bulk diffusion [26], and enhancing the catalytic lifetime. Nanotubes with lengths of several tens of micrometers were obtained on oxygen plasma treated samples (SEM image in Fig. 1c). The evaluation of the acquired length distribution in Fig. 1d yielded a median of 2.9 μm, while the third quartile L_{Q3} increased from 1.9 μm for the untreated catalyst to 13.3 μm for the samples with catalyst treated by oxygen plasma. However, the obtained CNTs of a few ten micrometers in length are significantly bent (see Fig. 1c), supposedly due to the incorporation of carbon 5- and 7-rings into the CNT lattice [27]. The increased CNT average length was also accompanied by an increase of diameters and spectral line widths which will be discussed in more detail below.

In the next step, we investigated the influence of the synthesis temperature and the methane flow rate on the CNT density. To this end, we performed CNT synthesis on Si/SiO_2 substrates with a fixed concentration of the catalyst solution and temperatures between 700 and 850 °C (in steps of 50 °C) as well as for methane flows rates of 0.16, 0.37, 0.58, and 1.0 slm at a fixed methane/hydrogen flow rate ratio of 1.33. For each growth condition, several SEM images of equal sample areas were examined at random positions of the substrate and the CNT density was determined by CNT counting. The results are summarized in Fig. 2. The data points represent the mean density whereas the error bars give the highest and lowest densities determined from individual SEM images of a given